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Chemical Specific. Volume 2
Control of Accidental Releases of Ammonia

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ABSTRACT

The accidental releases of a toxic chemical at Bhopal, India in 1984 was a milestone in creating an increased public awareness of toxic release problems. As a result of other, perhaps less dramatic incidents in the past, portions of the chemical industry were aware of this problem long before these events. These same portions of the industry have made advances in this area. Interest in reducing the probability and consequences of accidental toxic chemical releases that might harm workers within a process facility and people in the surrounding community prompted the preparation of this manual and a planned series of companion manuals addressing accidental releases of toxic chemicals.

Ammonia has an IDLH (Immediately Dangerous to Life and Health) concentration of 500 ppm, which makes it an acute toxic hazard. Reducing the risk associated with an accidental release of ammonia involves identifying some of the potential causes of accidental releases that apply to the process facilities that use ammonia. In this manual, examples of potential causes are identified as are specific measures that may be taken to reduce the accidental release risk. Such measures include recommendations on plant design practices, prevention, protection and mitigation technologies, and operation and maintenance practices. Conceptual cost estimates of example prevention, protection, and mitigation measures are provided.

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SECTION 1
INTRODUCTION

1.1 BACKGROUND

The consequences of a large release of a toxic chemical can be devastating. This was clearly evidenced by the release of a cloud of toxic methyl isocyanate in Bhopal, India on December 3, 1984, which killed approximately 2,000 people and injured thousands more. Prior to this event, there had been other, perhaps less dramatic, releases of toxic chemicals, but the Bhopal incident precipitated the recent public concern for the integrity of process facilities which handle hazardous materials.

Recognizing the fact that no chemical plant is free of all release hazards and risks, a number of concerned individuals and organizations have contributed to the development of loss prevention as a recognized specialty area within the general realm of engineering science. Interest in reducing the probability and consequences of an accidental release of anhydrous ammonia prompted the preparation of this manual. This manual is part of a series of manuals which addresses the prevention and control of a large release of any toxic chemical. The subjects of the other manuals planned for the series include

- A user's guide,
- Prevention and protection technologies,
- Mitigation technologies, and
- Other chemical specific manuals such as this one.

The manuals are based on current and historical technical literature, and they address the design, construction, and operation of chemical process facilities where accidental releases of toxic chemicals could occur. Specifically, the user's guide is intended as a general introduction to the subject of toxic chemical releases and to the concepts which are discussed in more detail in the other manuals. Prevention technologies are applied to the design and operation of a process to ensure that primary containment is not breached. Protection technologies capture or destroy a toxic chemical involved in an incipient release after primary containment has been breached but before an uncontrolled release occurs. Mitigation technologies reduce the consequences of a release once it has occurred.

Historically, there have been several major releases of anhydrous ammonia in the past fifteen years involving numerous injuries and a number of fatalities. Primary sources of these releases include pressurized pipeline ruptures, failed storage tanks, and road tanker accidents.

1.2 PURPOSE OF THIS MANUAL

The purpose of this manual is to provide technical information about anhydrous ammonia with specific emphasis placed on the prevention of accidental releases of this chemical. This manual addresses technological and procedural issues, related to release prevention, associated with the storage, handling, and process operations involving ammonia. (Note: Throughout this manual, "ammonia" refers only to anhydrous ammonia and not to aqueous or "aqua" ammonia.)

This manual is intended as a summary manual for persons charged with reviewing and evaluating the potential for releases at facilities that use, store, handle, or generate ammonia. It is not intended as a specification manual, and the reader is often referred to additional technical manuals and other information sources for more complete information on the topics discussed. Other sources of information include manufacturers and distributors of ammonia in addition to technical literature on design, operation, and loss prevention in facilities which handle toxic chemicals.

1.3 USES OF ANHYDROUS AMMONIA

Anhydrous ammonia (NH_3) is a significant commodity chemical, produced by the reaction of hydrogen and nitrogen over a catalyst. The dominant use of this chemical is in the fertilizer industry which accounts for nearly 80% of all ammonia produced (1). The direct application of ammonia to the soil is, in fact, the largest single use of the chemical. The primary industrial uses of ammonia are as a raw material in the manufacture of nitric acid and as the starting material in the production of a number of commercially important synthetic materials.

Numerous references in the technical literature provide information on both the manufacture and uses of anhydrous ammonia. In addition to the primary uses mentioned above, ammonia has many other minor uses in a wide variety of industries. Some of the more common uses include neutralization (especially the treatment of acidic wastes), extraction, refrigeration, water purification, the preparation of cleaners and detergents, pulp and paper manufacture, and food and beverage treatment.

1.4 CONTENTS OF THIS MANUAL

The five sections of this manual present the relevant issues associated with the prevention of an accidental release of anhydrous ammonia to the atmosphere. The physical, chemical, and toxicological properties of ammonia which create or enhance the hazards of an accidental release are presented in Section 2. In Section 3, the manufacture, consumption, and storage of ammonia are discussed, and the release hazards associated with these operations are identified. Next, potential causes of releases, including those identified in Section 3, are summarized in Section 4. Finally, Section 5 contains detailed information about hazards prevention and control. Topics included in this section are process and physical plant designs, protection and mitigation technologies, operating and maintenance practices, and illustrative costs.

SECTION 2
CHEMICAL CHARACTERISTICS

This section describes the physical, chemical and toxicological properties of anhydrous ammonia as they relate to accidental release hazards.

2.1 PHYSICAL PROPERTIES

At atmospheric temperatures and pressures, anhydrous ammonia is a pungent, colorless gas. It may easily be compressed or cooled to a colorless liquid. Its more important physical and chemical properties are presented in Table 2-1.

Pure liquid ammonia is lighter than water, and pure gaseous ammonia is lighter than air. Because of this latter property, a cloud of pure ammonia gas will be buoyant and rise into the atmosphere. However, depending on the pressure and temperature, air-ammonia mixtures which are denser than air may also be formed. For example, air which is adiabatically saturated with ammonia (6.1 wt%) has a density that is 1.35 times the density of air at ambient conditions (6). Hence, a saturated air-ammonia mixture may not disperse very readily and remain close to the ground. Water vapor may also condense out of an air-ammonia mixture, from the cooling effect of evaporating ammonia, causing fog. Because of the higher specific gravity of the cooled air, this fog could spread laterally over the ground (6). Regardless of the temperature and pressure, all air-ammonia mixtures containing more than 45 wt% ammonia are lighter than air (6).

Liquid anhydrous ammonia has a large coefficient of expansion. Hence, an overpressurization hazard exists if storage vessels have insufficient expansion space or if pipelines full of liquid ammonia may be sealed on both ends. In these situations, thermal expansion of the liquid with an increase in

TABLE 2-1. PHYSICAL PROPERTIES OF ANHYDROUS AMMONIA

		Reference
CAS Registry Number	07664-41-7	
Chemical Formula	NH_3	
Molecular Weight	17.03	
Normal Boiling Point	-28.17 °F @ 14.7 psia	1
Melting Point	-107.93 °F	1
Liquid Specific Gravity (H_2O=1)	0.6815 @ -27.7 °F	1
Vapor Specific Gravity (air=1)	0.5970 @ 32 °F	1
Vapor Pressure	128.8 psia @ 70 °F	1
Vapor Pressure Equation	$\log Pv = A - \frac{B}{T+C}$ where: Pv = vapor pressure, mm Hg T = temperature, °C A = 7.36050, a constant B = 926.132, a constant C = 240.17, a constant	2
Liquid Viscosity	0.255 cp @ -33.5 °C	2
Solubility in Water at 1 atm, wt. %	32 °F 42.8 50 °F 33.1 68 °F 23.4 86 °F 14.1	3
Specific Heat at Constant Volume (vapor)	0.38 Btu/(lb- °F) @ 32 °F	4

(Continued)

TABLE 2-1 (Continued)

		Reference
Specific Heat at Constant Pressure (vapor)	0.5 Btu/(lb-°F) @ 32 °F	4
Specific Heat at Constant Pressure (liquid)	1.10 Btu/(lb-°F) @ 32 °F	4
Latent Heat of Vaporization	588.2 Btu/lb @ -27.7 °F	1
Liquid Surface Tension	23.4 dynes/cm @ 52 °F	5
Additional properties useful in determining other properties from physical property correlations:		
Critical Temperature	270.32 °F	1
Critical Pressure	1639.1 psia	1
Critical Density	14.66 lb/ft^3	4

temperature can result in containment failure from the hydrostatic pressure exerted by the liquid.

The flammability range of ammonia in air at atmospheric pressure is from 16% to 25% ammonia by volume, while in oxygen the range is from 15% to 79% by volume (3). Increasing the temperature and pressure of the ammonia broadens the flammability range. Although the minimum ignition temperature for a mixture within the flammability limits is relatively high at 1562 °F (7), it is possible for ammonia to burn or explode under some conditions such as a large and intense source of ignition combined with a high concentration of ammonia gas (8). The presence of oil or a mixture of ammonia with other flammable substances will also increase the fire hazard. It has further been reported that the presence of iron appreciably decreases the ignition temperature (8).

Ammonia is readily absorbed in water to make ammonia liquor (ammonium hydroxide or aqua ammonia). The dissolution of ammonia in water is accompanied by relatively large heats of solution. Approximately 938 Btu of heat is evolved when 2.2 lb of ammonia gas is dissolved in water (3). The solubility of ammonia in water at various temperatures is given in Table 2-1.

2.2 CHEMICAL PROPERTIES AND REACTIVITY

Pure ammonia is a very stable compound under normal conditions; even slight dissociation to hydrogen and nitrogen does not occur at atmospheric pressure until temperatures of 840-930 °F are reached (7). The products of complete combustion of ammonia are neither toxic nor hazardous, since they are nitrogen and water.

Ammonia is a highly reactive chemical, forming ammonium salts with inorganic and organic acids. Ammonia reacts with chlorine in dilute solution to give chloramines, an important reaction in water purification (3). Because of the alkaline characteristics of ammonia it is also used as a neutralizing agent in a number of processes.

It has been reported that gold, silver, and mercury are each capable of reacting with ammonia to form explosive compounds (1). Other explosive materials which can be formed include metal hydrazides which are produced from the reaction of alkali metals and liquid ammonia. Acetylides, which are highly explosive in the dry state, are formed in the presence of ammonia solutions of copper, mercury or silver salts (1).

Most common metals do not react with dry ammonia. However, when mixed with very small amounts of water or water vapor, ammonia will vigorously attack copper, silver, zinc, and many alloys, especially those containing copper (9).

2.3 TOXICOLOGICAL AND HEALTH EFFECTS

Depending on the concentration, the effects of exposure to ammonia gas range from mild irritation to severe corrosion of sensitive membranes of the eyes, nose, throat, and lungs (3). Because of the high solubility of ammonia in water, it is particularly irritating to moist skin surfaces. A concentration of 500 ppm has been designated as the IDLH concentration (Immediately Dangerous to Life and Health), which is based on a 30-minute exposure. Table 2-2 presents a summary of some of the relevant exposure limits for ammonia gas (10).

The predicted human health effects from increasing concentrations of ammonia gas are summarized in Table 2-3 (1,3). Because the pungent odor of ammonia is immediately recognizable at low concentrations, it is highly unlikely that any individual would become overexposed unknowingly. Ammonia is not a cumulative metabolic poison; ammonium ions are actually important constituents of living systems. However, inhalation of high levels of ammonia gas may have fatal consequences as a result of the spasm, inflammation and edema of the larynx and bronchi, chemical pneumonitis and pulmonary edema (11). Exposure of the eyes to high concentrations may result in ulceration of the conjunctiva and cornea and destruction of all ocular tissues (11).

Contact of the skin with liquid ammonia may result in severe injury by freezing the tissue, since liquid ammonia vaporizes rapidly when released to the atmosphere and will absorb heat from any substance it contacts. If the skin is moist, it may also cause severe burns from the caustic action of the ammonium hydroxide produced.

TABLE 2-2. EXPOSURE LIMITS FOR ANHYDROUS AMMONIA

Exposure Limit	Concentration (ppm)	Description	Reference
IDLH	500	The concentration defined as posing an immediate danger to life and health (i.e., causes irreversible toxic effects for a 30-minute exposure).	10
PEL	50	This concentration was determined by the Occupational Safety and Health Administration (OSHA) to be the time-weighted 8-hour exposure limit which should result in no adverse effects for the average, healthy, male worker.	10
LC_{LO}	30,000	This concentration is the lowest published lethal concentration for a human over a 5-minute exposure.	10
TC_{LO}	20	This concentration is the lowest published concentration causing toxic effects (irritation).	10

TABLE 2-3. PREDICTED HUMAN HEALTH EFFECTS OF EXPOSURE TO VARIOUS CONCENTRATIONS OF ANHYDROUS AMMONIA (1,3)

ppm	Effect
5	Least perceptible odor
20-50	Readily detectable odor
40	A few individuals may suffer slight eye irritation
100	Noticeable irritation of eyes and nasal passages after a few minutes exposure
150-200	General discomfort and eye tearing; no lasting effect from short exposure
400	Severe irritation of the throat, nasal passages, and upper respiratory tract
700	Severe eye irritation; no permanent effect if the exposure is limited to less than 1/2 hour
1700	Serious coughing, bronchial spasms, burning and blistering of the skin; less than 1/2 hour of exposure may be fatal
5000-10000	Serious edema, strangulation, asphyxia, rapidly fatal
10000	Immediately fatal

SECTION 3

FACILITY DESCRIPTIONS AND PROCESS HAZARDS

This section contains brief descriptions of the processes and facilities for the manufacture, consumption, and storage of anhydrous ammonia in the United States. The purpose of this section is to identify major hazards associated with these facilities which may directly or indirectly cause accidental releases. Measures taken for the prevention of these hazards are discussed in Section 5.

3.1 MANUFACTURE (3,12)

Anhydrous ammonia is prepared by the reaction of hydrogen and nitrogen (the "synthesis" or "syn" gas) in the presence of a catalyst at elevated temperatures and pressures. The manufacturing process consists of three basic steps: synthesis gas preparation, purification, and ammonia synthesis. The first step involves the production of hydrogen and the introduction of the stoichiometric amount of nitrogen. In the second step, catalyst poisons (carbon dioxide, carbon monoxide, and water) are removed from the synthesis gas. The third step includes the catalytic fixation of nitrogen at high temperatures and pressures and recovery of the ammonia. The specific processes used by the numerous producers of ammonia primarily differ in the source of hydrogen for synthesis gas and the temperature and pressure of the ammonia synthesis loop.

The main sources of hydrogen in modern ammonia plants are coal, petroleum fractions, and natural gas, with the latter being the principal source in commercial practice. In general, the most economic feedstock has the highest hydrogen to carbon ratio. The two hydrogen generation techniques used for processing these raw materials are partial oxidation (reaction with oxygen) and steam reforming (reaction with steam). Of these, steam reforming is the more widely used process; partial oxidation processes are employed where steam-reformable feeds are not available or in special situations where favorable economic conditions exist.

Figure 3-1 is a typical process diagram for the production of ammonia by steam reforming. The first step in the preparation of the synthesis gas is desulfurization of the hydrocarbon feed. This is necessary, because sulfur poisons the nickel catalyst (albeit, reversibly) in the reformers, even at very low concentrations. Steam reforming of hydrocarbon feedstock is carried out in the primary and secondary reformers. The primary reformer is a refractory-lined furnace which contains vertically suspended tubes filled with a nickel-based catalyst. In the primary reformer, the feed reacts with steam to produce hydrogen gas and carbon monoxide. Some of the carbon monoxide also reacts with steam in the "shift conversion" reaction to produce carbon dioxide and hydrogen. The secondary reformer is a refractory-lined pressure vessel which contains additional reforming catalyst. Primary reformer effluent gas is mixed with air prior to entering the secondary reformer. This serves a two-fold purpose; it supplies the stoichiometric amount of nitrogen, and it supplies oxygen for combustion which supplies the heat required for the reforming reaction.

After passing through waste heat boilers, the syn gas enters the purification stage. Regardless of the hydrogen generation technique used, the unpurified syn gas contains carbon oxides which deactivate the ammonia synthesis catalyst and must be removed. In the shift converters, carbon monoxide is catalytically converted to carbon dioxide, which is removed more easily than CO, and hydrogen gas. The next purification step is the removal of carbon dioxide. Commercial processes generally involve absorbing the gas into a solvent under pressure and then recovering the solvent in a stripping column. The final purification step involves removal of the residual carbon monoxide and carbon dioxide in a methanator and, in some plants, cryogenic purification. In the methanator, CO and CO_2 are catalytically converted to methane which passes through the ammonia synthesis loop as an inert. The

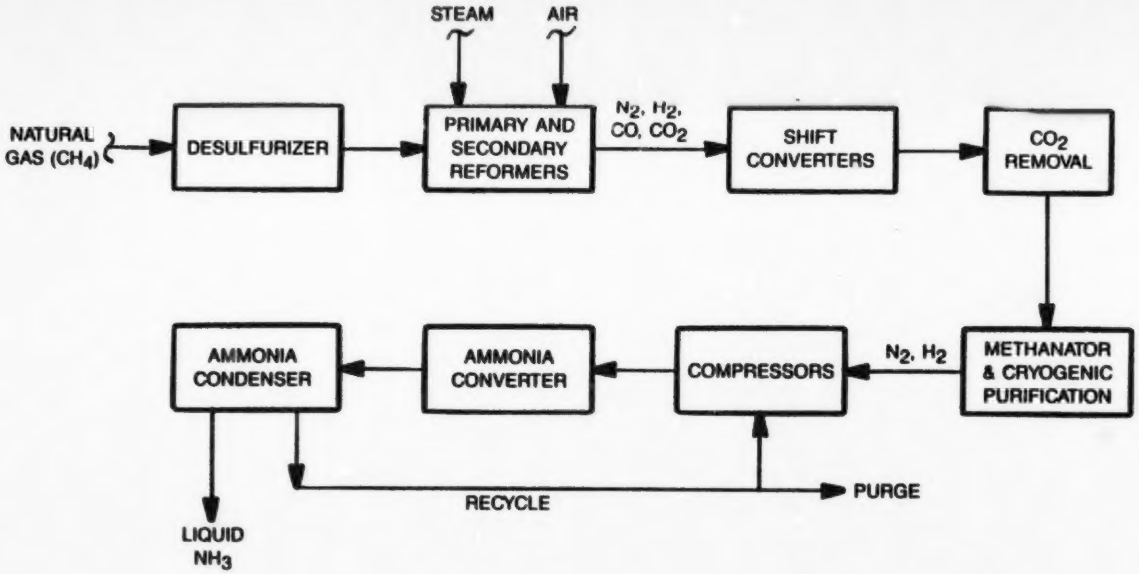

NATURAL GAS (CH_4)
DESULFURIZER
STEAM
AIR
PRIMARY AND SECONDARY REFORMERS
N_2, H_2, CO, CO_2
SHIFT CONVERTERS
CO_2 REMOVAL
METHANATOR & CRYOGENIC PURIFICATION
N_2, H_2
COMPRESSORS
AMMONIA CONVERTER
AMMONIA CONDENSER
LIQUID NH_3
RECYCLE
PURGE

Figure 3-1. Conceptual diagram of typical ammonia production process.

purpose of cryogenic purification is to remove the excess nitrogen added to the secondary reformer. This is done to avoid excessive loss of hydrogen and excessive compression costs in the ammonia synthesis loop.

The purified syn gas next flows to the final production stage which is ammonia synthesis and recovery. The first step is compression of the syn gas. Synthesis pressures range from 2,000 to 10,000 psi depending on the quality of the syn gas and certain other conditions, such as production requirements per converter (12). Almost without exception, all modern large-scale ammonia plants employ steam-driven centrifugal compressors for synthesis service. One of the advantages of centrifugal compressors is that a minimal amount of lubricating oil is required, as this material causes problems in the synthesis loop. For smaller plants, under 600 tons/day, reciprocating compressors are still used.

Basically, there are two classes of ammonia converters, tubular and multiple bed. The tubular bed reactor is limited in capacity to a maximum of about 544 tons/day (3). In most reactor designs, the cold inlet synthesis gas flows through an annular space between the converter shell and the catalyst cartridge. This maintains the shell at a low temperature, minimizing the possibility of hydrogen embrittlement which can occur at normal synthesis pressures. The inlet gas is then preheated to synthesis temperature by the exit gas in an internal heat exchanger, after which it enters the interior of the ammonia converter which contains the promoted iron catalyst.

Gas recirculation in the ammonia synthesis section is necessary, because only 9-30 percent conversion is obtained per pass over the catalyst (12). The synthesis loops are generally of two types. One type recovers ammonia product after makeup gas-recycle compression and the other recovers ammonia product before recycle compression. Inerts entering with the makeup gas are removed with a purge stream. The ammonia is recovered by condensation which requires refrigeration. Since anhydrous ammonia is readily available, it is normally used as the refrigerant.

Ammonia release hazards in the production process described above occur in the latter part of the process, specifically in the ammonia synthesis loop, where ammonia is present in relatively pure form. The types of equipment in the synthesis loop include large compressors, the ammonia converter, the ammonia condenser (plus ammonia refrigeration equipment), and the associated piping and instrumentation. Some previously reported and other possible causes of equipment failure in this section include the following (13,14):

- Compressors
  - severe vibrations on compressor and/or turbine,
  - rotor failed,
  - compressor thrust collar broke,
  - coupling bolts failed,
  - compressor seal failed,
  - broken blades on turbine,
  - reduction gear bearing failed, and
  - compressor O-ring failed.

- Ammonia Converter
  - cracking induced by thermal shock,
  - hydrogen-induced cracking,
  - loss of feed control, and
  - overheating of the catalyst bed.

- Heat exchangers (including condensors)
  - tube failures, and
  - loss of cooling resulting in overpressure.

- Piping and instrumentation
  - relief valve did not reseat,
  - valve packing was blown,
  - improper materials of construction, and
  - rupture due to corrosion/erosion effects.

Of the four major compressors in ammonia production, the service performed by the synthesis gas compressor is the most demanding (13). It discharges at the highest pressure, requires the most horsepower, has an intricate seal oil system, has the most compressor/turbine bodies, and operates at a relatively high speed. If the ammonia is condensed from the synthesis loop prior to compression of the syn gas, the ammonia content in the compressor will be relatively low. However, if the ammonia is compressed with the syn gas prior to recovery, a failure in the syn gas compressor is a significant release hazard.

Ammonia plants are subjected to a thermal cycle with each shutdown and start-up. During planned shutdowns, the plant comes down at a slow, controlled rate. However, other shutdowns are unplanned, and some plants tend to come down rather quickly in these situations. The effect of rapidly reducing the process gas temperature in the ammonia converter is the creation of high thermal stresses. This thermal cycle is a primary cause of surface cracks in the walls and outlet of the converter (14). A second effect of cooling a thick-wall component in high-temperature, high-pressure hydrogen service is to supersaturate the metal with respect to hydrogen. The excess hydrogen is trapped in the metal and collects in discontinuities, such as small cracks or non-metallic inclusion, and exerts pressures high enough to initiate cracks. Hydrogen-induced cracking may therefore magnify the effect of thermal stress to produce hazardous internal cracks.

Overheating the ammonia converter could result in uncontrollable combustion reactions or explosions with the consequent physical breakdown of the reactor vessel by thermal fatigue or overpressure. Possible causes of overheating include the following:

- Poor heat distribution within the reactor bed, resulting in hot spots;
- Overheating raw materials before they enter the ammonia converter; and

- Loss of composition or quantity control of raw material feeds.

The condenser, piping, and instrumentation hazards listed above are not specific to the ammonia production process. Other possible causes of release from these components are covered in Section 4. The hazards associated with the use of ammonia as a refrigerant are discussed in Section 3.2.5.

3.2 PROCESSING AND CONSUMPTION

Because the uses of ammonia in the U.S. are many and diverse, the processes discussed in this section are limited to those which 1) represent the primary consumers of anhydrous ammonia, 2) are widespread but not large consumers of ammonia, or 3) are especially hazardous. Some of the numerous minor uses of ammonia which are not discussed include the following processes: manufacture of rubber, water purification, food and beverage treatment, the production of pulp and paper, the preparation of cleaners and detergents, and leather and textile treatment.

Ammonia is also used in the manufacture of many important industrial chemicals which are too numerous to discuss individually. Table 3-1 lists many of the industrial chemicals produced directly from anhydrous or aqueous ammonia (15). In many cases, the primary release hazards in the production processes are associated with the ammonia storage, feed, and recovery systems. The processes discussed in the following subsections provide specific examples of the general hazards of ammonia processing, while the specific hazards of ammonia storage are discussed in Section 3.4.

3.2.1 Fertilizer Production (16,17,18)

The fertilizer industry is, by far, the largest consumer of anhydrous ammonia in the United States, accounting for 70-80 percent of all ammonia

TABLE 3-1. ANHYDROUS AND AQUEOUS AMMONIA PRODUCTS (15)

ammonium acetate
ammonium adipate
ammonium benzoate
ammonium bicarbonate
ammonium bifluoride
ammonium binoxalate
ammonium bisulfate
ammonium bitartrate
ammonium tetraborate
ammonium bromide
ammonium carbonate
ammonium chloride
ammonium citrate
ammonium dichromate
ammonium fluoride
ammonium fluorosilicate
ammonium gluconate
ammonium iodide
ammonium molybdate
ammonium nitrate
ammonium oxalate
ammonium perchlorate
ammonium picrate
ammonium polysulfide
ammonium salicylate
ammonium stearate
ammonium sulfate
ammonium sulfide (hydrosulfide)
ammonium tartrate
ammonium thiocyanate
ammonium thiosulfate
ammonium paratungstate

urea
monoammonium phosphate
diammonium phosphate
nitric oxide
acrylonitrile
caprolactam
monomethylamine
dimethylamine
hexamethylenetetramine
trimethylamine
monoethanolamine
diethanolamine
triethanolamine
hydrogen cyanide
fatty nitrogen compounds (nitriles, amines, quaternary ammonium compounds)
boron nitride
calcium carbonate (precipitated from calcium chloride)
hydrazine
hydrogen (high purity)
lead hydroxide
lithium amide
methyl ethyl pyridine
sodamide
sodium cyanide
nitrogen dioxide
nitric acid

produced in the past decade. In fact, the largest single use of ammonia is its direct application as a fertilizer. The ammonia-based fertilizers produced in the greatest quantity include ammonium nitrate, ammonium sulfate, ammonium phosphates (mono- and di-), and urea. In addition, nitrogen solutions and mixed fertilizers are prepared which consist of combinations of the various products mentioned above along with fertilizers derived from elements other than nitrogen, e.g., phosphorus.

In the following paragraphs, the processes for the manufacture of the three ammonium salts and urea are briefly discussed, and the primary process hazards within the fertilizer industry are identified. In many cases, plants for the production of ammonia-based fertilizers are integrated with ammonia plants at the same facility, such that the hazards of ammonia production presented in the Section 3.1 would also exist at this type of installation.

Ammonium Nitrate--

Ammonium nitrate is produced by the neutralization of nitric acid with anhydrous ammonia in an atmospheric or pressurized reactor. Figure 3-2 is a flow diagram of a typical manufacturing process. The reaction of ammonia with nitric acid is strongly exothermic. The high heat of reaction causes flash vaporization of water with some ammonia and nitrate going overhead. The temperature of the solution in the neutralizer is controlled by regulated addition of the reactants and by removal of the heat. The reactor effluent is approximately 83 wt% ammonium nitrate. This product can be sold without further processing, or additional water can be evaporated to produce the salt in dry form.

The parts of the ammonium nitrate production process which present ammonia release hazards are between the ammonia feed (storage) tank and the reaction tank or neutralizer. Release hazards of ammonia storage are discussed in Section 3.4. The neutralizer is a high hazard area because it operates at elevated temperatures and pressures, and the neutralization reaction is extremely exothermic. Potential causes of a release include loss of feed control and loss of cooling.

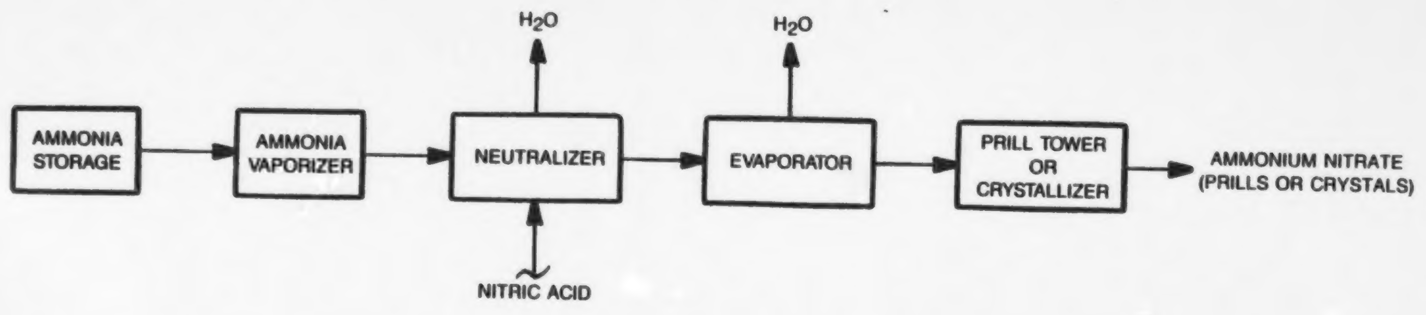

AMMONIA STORAGE
AMMONIA VAPORIZER
NEUTRALIZER
H_2O
NITRIC ACID
EVAPORATOR
H_2O
PRILL TOWER OR CRYSTALLIZER
AMMONIUM NITRATE (PRILLS OR CRYSTALS)

Figure 3-2. Conceptual diagram of typical ammonium nitrate process.

Both a loss of feed control and a loss of cooling would result in overheating of the reactor contents. Overheating may lead to overpressure if the vessel does not have adequate pressure relief devices, or if they fail to operate in the correct manner. In addition to causing excessive heat generation, a loss of feed control may also cause overpressure if the relief devices fail to activate. Reactor failure (rupture) could result from the development of temperatures or pressures which exceed design conditions.

Solid and molten NH_4NO_3 can be hazardous under certain conditions, e.g., when detonated and/or in the presence of an oxidizable substance. However, this property does not create a significant ammonia release hazard in the ammonium nitrate production process, because it is highly unlikely that these conditions will exist (especially prior to evaporation) in the parts of the process where ammonia is present. The explosive property of ammonium nitrate would, however, create a hazard with respect to an ammonia release if the storage facilities for the dry ammonium nitrate were located in close proximity to the ammonia storage tank.

Ammonium Sulfate--

Ammonium sulfate is produced by the reaction of by-product ammonia from various processes with sulfuric acid. Because of the limited number of by-product ammonia sources, ammonium sulfate is also produced by the neutralization of sulfuric acid with synthetic ammonia. (The same principles and practices are involved in the two procedures, but the synthetic raw materials give a purer product.) A typical process diagram for the production of ammonium sulfate from synthetic ammonia is shown in Figure 3-3. Anhydrous ammonia is dissolved in water and pumped to the neutralizer where it meets a stream of concentrated sulfuric acid (92-98% H_2SO_4). The solution of ammonium sulfate that forms is pumped into double-effect crystallizers. The ammonium sulfate crystals from the crystallizer are separated by centrifuging or filtering and are dried.

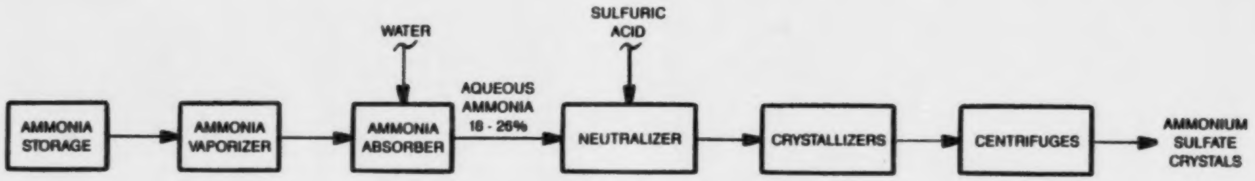

AMMONIA STORAGE
AMMONIA VAPORIZER
WATER
AMMONIA ABSORBER
AQUEOUS AMMONIA 18 - 26%
SULFURIC ACID
NEUTRALIZER
CRYSTALLIZERS
CENTRIFUGES
AMMONIUM SULFATE CRYSTALS

Figure 3-3. Conceptual diagram of typical ammonium sulfate process.

The ammonia release hazards in this process are only present between the storage/feed systems and the point where ammonia is absorbed in water to form the aqueous solution which is fed to the neutralizer. These hazards are not specific to the ammonium sulfate process and are discussed in other parts of this manual.

Ammonium Phosphate--

Although ammonium phosphate fertilizers are produced by several methods, the simultaneous ammoniation and granulation process is, by far, the predominant method. In this process, a rolling bed of recycled undersized ammonium phosphate particles is acidified by a spray of phosphoric acid which is immediately neutralized by ammonia injected beneath the surface of the bed through fixed spargers. Alternatively, the granulation process can be combined with a preneutralizer unit in which the phosphoric acid is first partially neutralized with ammonia in an agitated vessel. This process is shown in Figure 3-4. The heat of reaction results in a preneutralizer vessel temperature of about 240 °F and the evaporation of about 20% of the water present. The hot slurry is sufficiently fluid to be distributed over the rolling bed in the ammoniator-granulator. In either case, an excess of ammonia is required in the ammoniator to reach the required N:P_2O_5 ratio required. This excess is recovered by scrubbing the ammoniator-granulator off-gases with the incoming acid.

As in the production of the other two ammonium salts, the ammonia release hazards are present between the ammonia storage/feed systems and the preneutralizer. The hazards of ammonia storage and handling general to all ammonia processes (including heat exchangers, piping, and instrumentation) are discussed in other parts of this manual. As with the ammonium nitrate process, the neutralization of phosphoric acid is accompanied by a large heat of reaction, and thus a loss of feed control or reactor cooling could lead to overheating and/or overpressure, possibly resulting in reactor failure with a loss of containment of the contents.

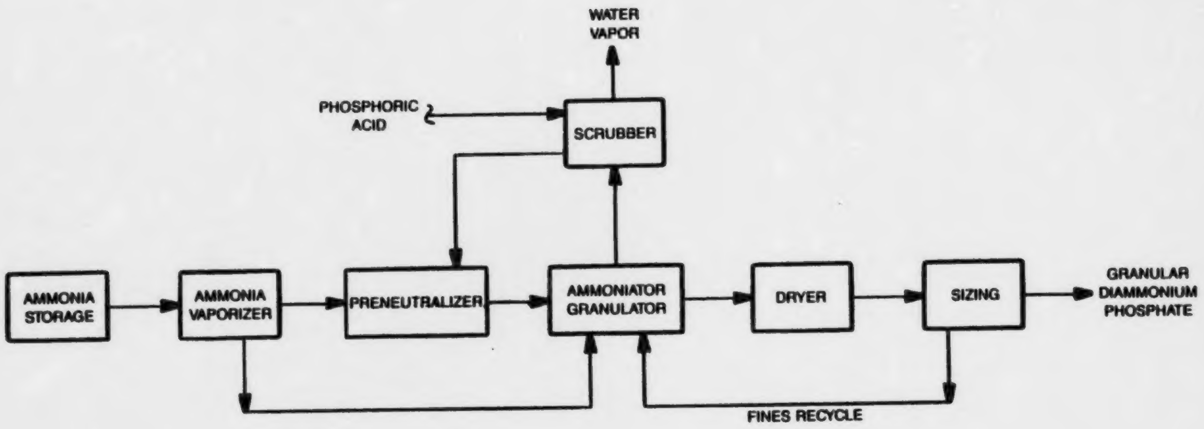

WATER VAPOR
PHOSPHORIC ACID
SCRUBBER
AMMONIA STORAGE
AMMONIA VAPORIZER
PRENEUTRALIZER
AMMONIATOR GRANULATOR
DRYER
SIZING
GRANULAR DIAMMONIUM PHOSPHATE
FINES RECYCLE

Figure 3-4. Conceptual of diagram typical diammonium phosphate process.

Urea--

Urea is indirectly produced by the exothermic reaction of anhydrous liquid ammonia and gaseous carbon dioxide at elevated temperatures and pressures. The initial reaction product is ammonium carbamate, which subsequently decomposes to produce urea and water. Urea plants are always built in conjunction with ammonia plants, so that both reactants are obtained from the ammonia synthesis operation.

Figure 3-5 is a typical flow diagram for the production of urea. The reaction is carried out with an excess (50-100%) of liquid anhydrous ammonia in a stainless steel- or lead-lined reactor at pressures ranging from 2000-5000 psig and temperatures of 250-380 °F. As the reaction does not go to completion, the unreacted gases must be separated from the reactor effluent by heating and decompression, after which they are either recycled to the reactor or utilized in another process. Total recycle of the reactants is the most common practice. In this process, the ammonia, carbon dioxide, and ammonium carbamate are separated from the reactor effluent in the low- and high-pressure decomposers. The low-pressure off-gas is condensed in the low-pressure absorber, and the liquid is pumped into the high-pressure absorber for absorption of the high-pressure decomposer gas. Unabsorbed excess ammonia from the high-pressure absorber is condensed in the ammonia condenser and recycled to the reactor, as is the concentrated carbamate solution recovered in the high-pressure absorber. The product stream leaving the decomposers is about 70% to 80% urea. This product can be used as is, or it can be further concentrated to a solid product.

In the urea manufacturing process, ammonia is present in relatively pure form in the ammonia recovery section (condenser and receiver), the feed system (storage, receiver, pump, and preheater), and the carbamate reactor. Of these, the reactor presents the only release hazards which are specific to the urea manufacturing process. Release hazards are significant because of the

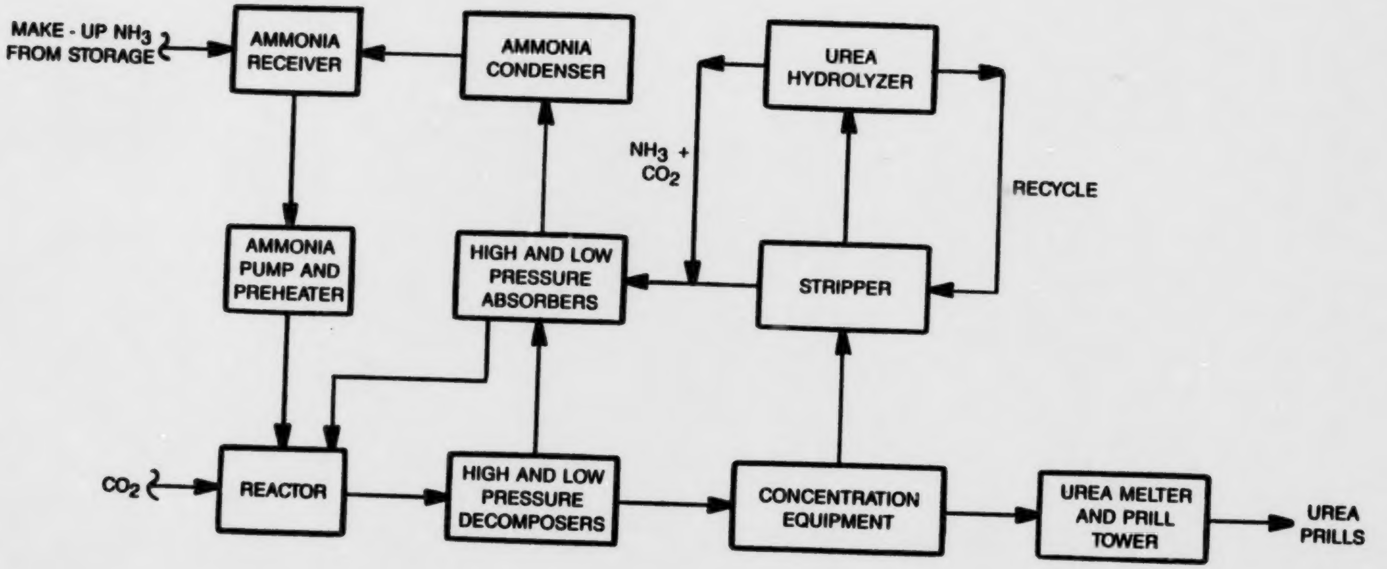

MAKE - UP NH_3
FROM STORAGE
AMMONIA RECEIVER
AMMONIA CONDENSER
UREA HYDROLYZER
NH_3 +
CO_2
RECYCLE
AMMONIA PUMP AND PREHEATER
HIGH AND LOW PRESSURE ABSORBERS
STRIPPER
CO_2
REACTOR
HIGH AND LOW PRESSURE DECOMPOSERS
CONCENTRATION EQUIPMENT
UREA MELTER AND PRILL TOWER
UREA
PRILLS

Figure 3-5. Conceptual diagram of typical urea manufacturing process.

high temperatures and pressures in the reactor, and because the reaction is highly exothermic. Therefore, a loss of cooling or feed control could result in overheating or overpressure with subsequent reactor fracture and the loss of containment of the reactants. Another hazard arises from the possibility that there will be an upset in the ammonia process resulting in unacceptable levels of impurities in the reactants. If, for example, the CO_2 were to contain more than about 2% (volume) nitrogen and hydrogen and was somehow mixed with air, an explosive gaseous mixture may result (19). High tensile steel is also susceptible to stress corrosion cracking by steam, hot water chlorides, sulfur compounds, and nitrates.

3.2.2 Nitric Acid Production (17,20)

Nitric acid, a major industrial chemical, is prepared by the oxidation of ammonia. Although its primary consumption is in the fertilizer industry, nitric acid is also the starting material for most of the nitrogen compounds used in the manufacture of explosives, which account for about 4-5 percent of all ammonia produced, in addition to being a raw material in the production of a large number of commercially important organic chemicals.

Although the specific operating details vary among the plants which produce nitric acid, they have in common the following three steps: oxidation of ammonia to nitric oxide (NO), oxidation of the nitric oxide to the dioxide (NO_2), and absorption of nitrogen oxides in water to produce nitric acid.

Figure 3-6 is a diagram of a typical nitric acid production process. Ammonia is evaporated and superheated before being mixed with preheated air. Since the explosive limit of ammonia is approached at concentrations greater than 12 mol% (at the conditions of this process), the ratio of ammonia to air in the feed is controlled in the range 9.5-10.5 mol% ammonia. This mixture flows to the ammonia converter where it is reacted on a platinum-rhodium gauze pad operating in the ranges of 1472-1760 °F and 0-120 psig. The reaction, which produces NO and H_2O, is extremely rapid and goes almost to completion.

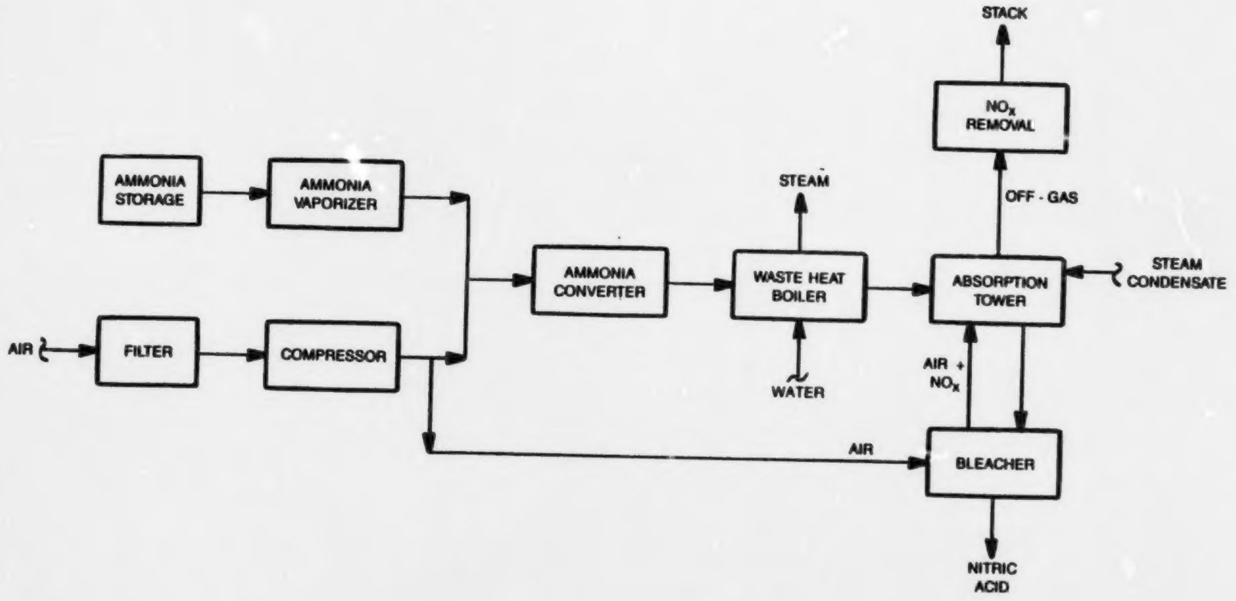

STACK
NOx REMOVAL
OFF - GAS
AMMONIA STORAGE
AMMONIA VAPORIZER
STEAM
AMMONIA CONVERTER
WASTE HEAT BOILER
ABSORPTION TOWER
STEAM CONDENSATE
AIR
FILTER
COMPRESSOR
WATER
AIR + NOx
AIR
BLEACHER
NITRIC ACID

Figure 3-6. Conceptual diagram of typical nitric acid production process.

The NO thus produced undergoes a slow homogeneous reaction with oxygen to yield nitrogen dioxide. The production of NO_2 is favored by relatively lower temperatures (below 300 °F). The hot effluent gas is therefore cooled by heat exchange with the feed gas and passes through low pressure boilers before entering the absorption towers. The pressure of the gas and the residence time in route to the absorption towers can be adjusted to effect the desired percentage oxidation of the NO. In the absorption towers, which may be spray towers, packed columns, or plate columns, the gas is scrubbed with weak acid and water (steam condensate). The normal grades of 45-65% HNO_3 are produced directly in the plant; these may be concentrated to 86-99% HNO_3 (fuming) by distillation under various conditions.

Ammonia release hazards specific to the nitric acid process are a loss of cooling or a loss of feed control to the ammonia converter. The realization of these hazards may result in overheating and/or overpressure of the reactor causing failure and release of the reactor contents. A loss of feed control is especially hazardous, because an explosive mixture which exceeds the flammability limits of ammonia may result.

3.2.3 Recovery of Ammonia from Refinery Waste Water (21,22)

In the petroleum industry ammonia is used as a solvent, a refrigerant, a corrosion inhibitor, and as a neutralizer of the acidic constituents of oil. Additionally, in some refineries, it is recovered as a salable product from sour water. This process is described below; refrigeration and neutralization processes are discussed in Sections 3.2.5 and 3.2.6, respectively.

Waste waters from several petroleum refining processes contain appreciable quantities of ammonia. Typical concentrations reported in the literature range from 3% to 10% by weight. The "WWT Process" is a patented process for treating these refinery wastes. The process recovers high-purity ammonia along with hydrogen sulfide and clean water suitable for reuse or for discharge. The larger WWT units produce more than 50 tons of anhydrous ammonia per day (21).

A typical WWT Process arrangement is shown in Figure 3-7. The feed consists of sour water from a degassing unit in which dissolved hydrogen, methane, and other light hydrocarbons are removed. The feed is pumped through a feed heater into a reboiler stripper column. In this column, the hydrogen sulfide is stripped overhead while the ammonia and water are removed as the bottoms product. The overhead product is high purity hydrogen sulfide which contains negligible ammonia. The bottoms product goes directly to a second reboiler stripper column. The bottoms from this column is "clean" water (typically <50 ppm NH_3 and <5 ppm H_2S) suitable for many in-plant reuse needs, while the overhead product is ammonia with small amounts of hydrogen sulfide and water. These constituents are removed in the ammonia purification section which consists of one or more scrubbing stages depending on the desired purity. The ammonia product is then compressed and condensed to salable anhydrous liquid ammonia. Alternatively, the ammonia product can be produced as high-purity aqueous ammonia solution which eliminates the need for an ammonia compressor. Because the ammonia is handled in solution, the production of aqueous ammonia may be less hazardous than the production of anhydrous ammonia. If there is no immediate use or sale for the ammonia recovered from the second stripper, it can be incinerated in a process furnace or special incinerator.

The potential hazards which may result in a large release of ammonia liquid or gas involve the latter portion of the process where ammonia is present in relatively pure form. This section of the process begins with the overhead product from the second stripper and ends with the final ammonia product storage. Included are the ammonia stripper and condenser; one or more H_2S scrubbers; product compressors, condensers and storage facilities; and associated piping and instrumentation. Process upsets specific to the WWT Process which may lead to a large release of anhydrous ammonia include:

- Overheating of the ammonia stripper from excess heat to the ammonia stripper reboiler or a sudden decrease in ammonia feed; and

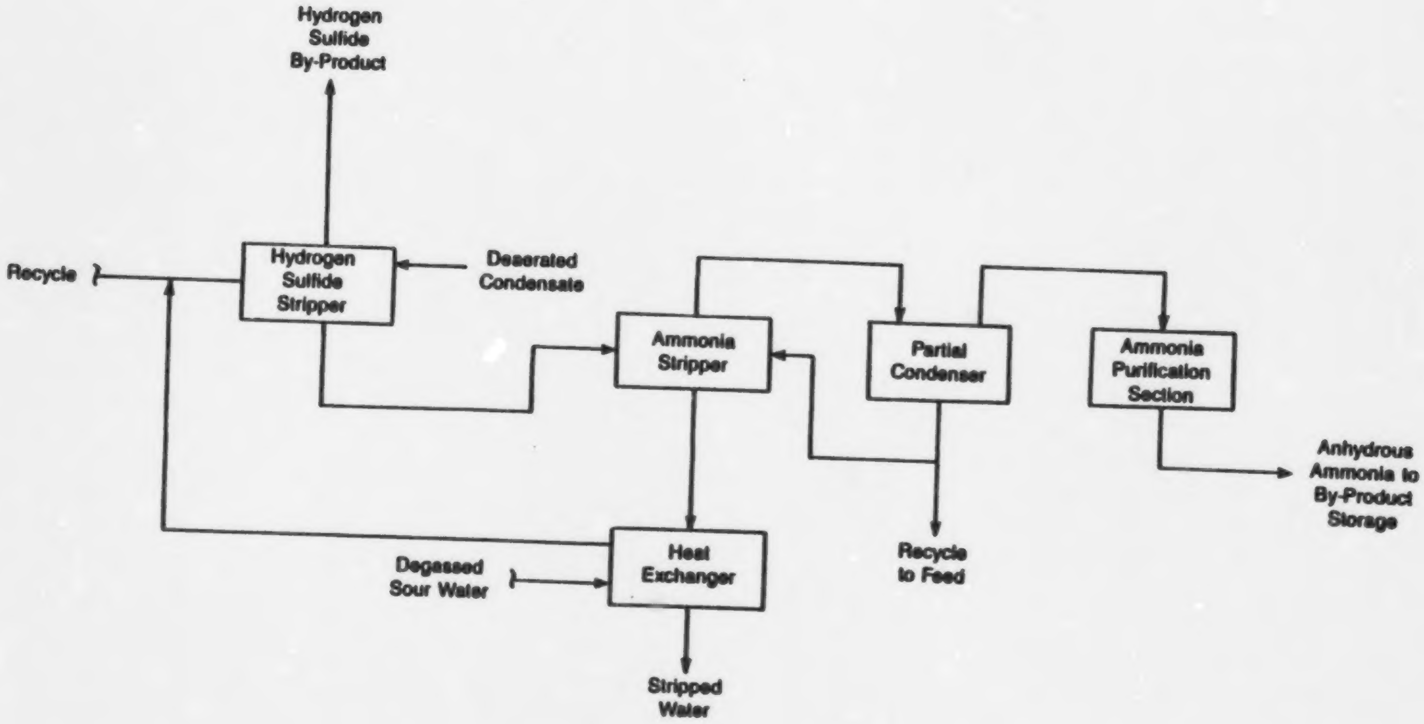

Hydrogen Sulfide By-Product
Recycle
Hydrogen Sulfide Stripper
Deaerated Condensate
Ammonia Stripper
Partial Condenser
Ammonia Purification Section
Anhydrous Ammonia to By-Product Storage
Recycle to Feed
Degassed Sour Water
Heat Exchanger
Stripped Water

Figure 3-7. Conceptual diagram of "WWT" waste water treatment process.

- Overheating of the ammonia condensers from a loss of cooling water.

These process upsets could potentially result in equipment failure from overpressurization. Additional hazards which are associated with the storage and transfer of anhydrous ammonia are discussed in Section 3.4, while general causes of equipment failure are discussed in Section 4.0.

3.2.4 The Use of Ammonia in the Production of Resins (16,17,23)

Anhydrous ammonia and ammonia derivatives (e.g., aqueous ammonia, nitric acid) are used in the production of a variety of resins and fibers. These resins are subsequently used in the manufacture of many commercially important products in the synthetic plastics, adhesives, coatings, and textiles industries. This market consumes between 8 and 10 percent of all ammonia produced in the U.S. By far, the greatest amounts go to the production of amino, acrylic, and polyamide (nylon) resins, polyurethanes, and linear polyesters (17).

The production of acrylonitrile (an acrylic resin) is one process which uses anhydrous ammonia directly as a reactant. The process, shown schematically in Figure 3-8, involves reacting a gaseous mixture of propylene, ammonia, and air in a ratio of 1.4:1.4:10 in the presence of a catalyst. The three reactants are fed to a fluidized bed reactor operating at a temperature of 750-950 °F and 5-30 psig pressure. The reactor effluent is scrubbed in a countercurrent absorber, and the organic materials are recovered from the absorber water by distillation. Hydrogen cyanide, water, light ends, and high boiling impurities are removed from the crude acrylonitrile by fractionation to produce specification acrylonitrile product. Because the conversion obtained on a once-through basis is high, no separation or recycling of unreacted raw materials is necessary. However, in another commercial process which does not have a high conversion, the unreacted ammonia is absorbed by a countercurrent flow of aqueous sulfuric acid to produce ammonium sulfate as a by-product (16).

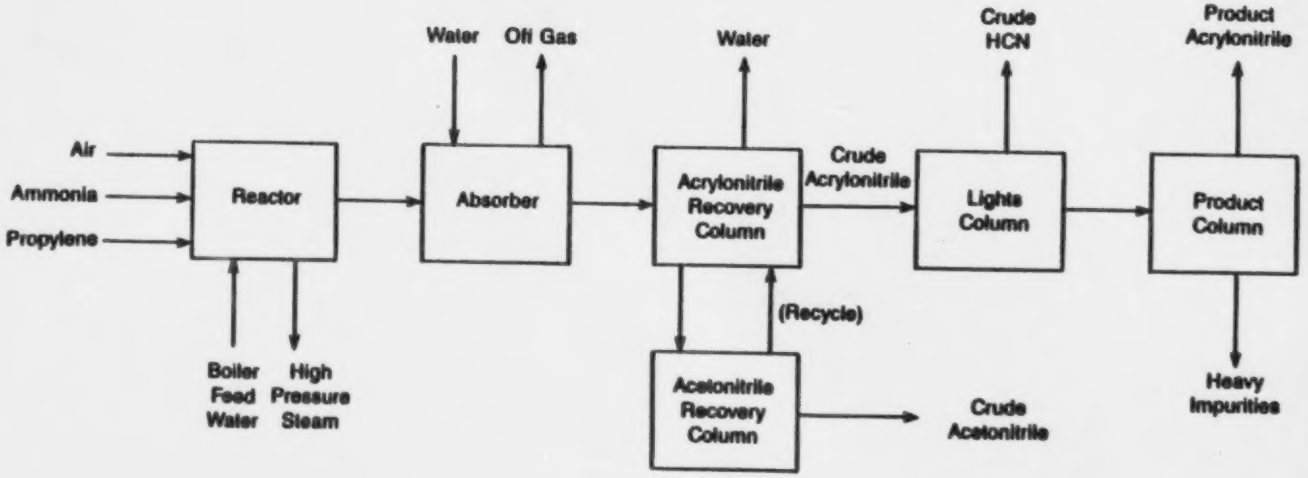

Air
Ammonia
Propylene
Reactor
Boiler Feed Water
High Pressure Steam
Water
Off Gas
Absorber
Water
Acrylonitrile Recovery Column
(Recycle)
Acetonitrile Recovery Column
Crude Acrylonitrile
Crude HCN
Lights Column
Crude Acetonitrile
Product Acrylonitrile
Product Column
Heavy Impurities

Figure 3-8. Conceptual diagram of typical acrylonitrile process.

Hazards which may lead to a large release of anhydrous ammonia in the acrylonitrile production process involve the portions of the process where ammonia is present in relatively pure form. Because no ammonia recovery is required, this only includes the section between the storage (feed) tank and the catalytic reactor. This section contains the storage tank, the ammonia vaporizer (usually a solenoid valve), feed preheater, piping to the reactor, a flow controller, and various other instrumentation. Possible causes of a hazardous release from any of these components are discussed in Sections 3.4 and 4.0. Process upsets, e.g., overheating from a loss of cooling water, are unlikely to lead to a large release of ammonia unless coupled with another event such as the loss of ammonia feed control. In the event of a reactor failure, this situation would allow excess ammonia to vent to the atmosphere.

3.2.5 The Use of Ammonia as a Refrigerant (14,24)

One of the predominant minor uses of ammonia (generally less than 2% of annual production) is as a refrigerant. Because of its toxic properties, ammonia is primarily suitable for industrial applications where a refrigerant leak will not cause occupant discomfort. For this reason also, it is extremely important that ammonia equipment and piping are arranged so that components may be easily isolated for repair, replacement, or overhaul.

Anhydrous ammonia is used in vapor compression systems. These systems vary from simple single-stage refrigeration cycles to complex multistage compound or cascade cycles depending on the application.

Figure 3-9 shows the basic refrigeration cycle for a single-stage system. The four basic components are the compressor, condenser, expansion valve, and evaporator. High pressure liquid ammonia flows from the condenser receiver through an expansion valve to the evaporator. Here, heat is absorbed from the fluid to be cooled, and the ammonia boils. The gaseous ammonia is then

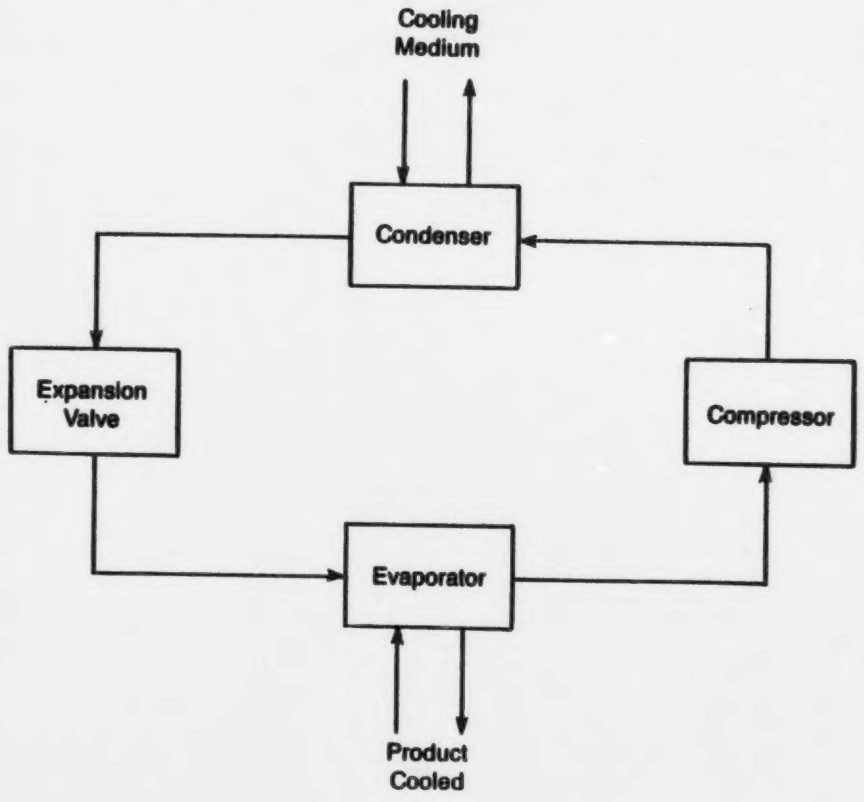

Cooling
Medium
Condenser
Expansion
Valve
Compressor
Evaporator
Product
Cooled

Figure 3-9. Conceptual diagram of basic vapor compression refrigeration cycle.

compressed to a temperature and pressure at which the superheated vapor can be condensed by the cooling media available for use in the condenser. The refrigeration cycle thus involves two pressures, high and low, to enable a continuous process which produces the desired cooling effect.

Possible causes of a hazardous release from an ammonia refrigeration system include the following:

- Overpressurization, and
- Equipment damage.

Failure of the refrigeration compressor stops circulation of refrigerant through the evaporator. If the flow of the fluid being cooled is not stopped, the pressure in the evaporator will rapidly rise causing the relief valves to open. If these valves are not vented to a closed system, ammonia will be released to the atmosphere. A similar situation can occur if cooling water to the condenser is lost. Again, relief valves on the condenser would open as the pressure exceeds the limit.

Catastrophic equipment failure could result in a large release of ammonia liquid and/or gas. Because refrigeration systems operate at greater than atmospheric pressure, ammonia will quickly escape from the source of a release.

The primary cause of refrigeration equipment problems is lack of adequate precautions during the design, construction and installation of the system (24). The components of the refrigeration system which are especially vulnerable to damage from start-up procedures and process upsets include machinery with moving parts such as pumps and compressors. Abnormally high process temperatures may occur either during start-up or process upsets. Provision must be made for this possibility, for it can cause damaging thermal stresses on refrigeration components and excessive boiling rates in evaporators, causing liquid to carry over and damage the compressor.

It is also important that the system is kept internally clean during installation. This is because ammonia is a powerful solvent, and dirt, scale, sand, or moisture remaining in the pipes, valves and fittings will be swept along with the suction gas to the compressor, where it is potentially harmful to the bearings, pistons, cylinder walls, valves and lubricating oil. When a compressor is run for the first time, moving parts are often scratched (24). Although damage is only minor in the beginning, scratches may progress until they seriously affect the operation of the compressor or render it inoperative (24).

3.2.6 Neutralization of Acidic Waste Streams with Ammonia (25)

A variety of industrial processes generate waste streams which are acidic in nature. For example, sulfuric acid is used in lead-acid battery manufacturing processes resulting in waste streams with a pH of around 2 (25). Regardless of the source, acidic wastes must usually be neutralized prior to further treatment or discharge. Owing to its alkaline properties, anhydrous ammonia is often used as the neutralizing agent for these wastes.

The neutralization process itself is relatively simple. In most processes, anhydrous ammonia is vaporized through a solenoid valve as it leaves a pressurized storage tank. The gaseous ammonia flows through carbon steel piping to a neutralization drum, pit, or tank where it is sparged into the waste solution. The ammonia may be piped directly into the bottom of the tank or sent through a vertical feed pipe which is immersed in the solution. The quantity of ammonia fed is automatically controlled by either wastewater flowrate or pH.

The hazards associated with the neutralization process primarily involve the ammonia storage system. These hazards are general to all ammonia facilities and are discussed in Section 3.4. The only other part of the process where ammonia is present in nearly pure form is the feed system. However, a failure in this system which causes too much or too little ammonia to be fed would probably not result in a large release of anhydrous ammonia. A slight overpressurization potential would exist if the neutralization tank were a closed system without a pressure relief device or had insufficient relief piping volume to handle any excess gas which is not absorbed in solution. However, because ammonia is so soluble in water, it would take a rather large quantity to saturate an aqueous waste stream.

One other consideration in neutralization systems is the use of suitable materials of construction for the tank and any ammonia piping which comes into contact with the waste solution. Improper materials of construction may lead to corrosion and possible equipment failure. The type of container used as well as the materials of construction will depend on the characteristics of the waste. A corrosion hazard also exists if precautions are not taken to prevent backflow of the waste into the carbon steel ammonia piping.

3.2.7 The Manufacture of Hydrogen Cyanide (17)

Anhydrous ammonia is a raw material in the manufacture of hydrogen cyanide (HCN). This chemical is a colorless, volatile liquid that is highly flammable and very toxic. All production of HCN in the United States is based on the continuous catalytic reaction of air, ammonia, and methane.

Figure 3-10 is a block diagram of a typical hydrogen cyanide manufacturing process. In this process, ammonia, methane, and air are preheated to about 750-950 °F, mixed, and sent to a packed bed reactor. The reactor is typically packed with a catalytic wire gauze composed of platinum, and a normal reaction temperature of about 2000-2200 °F is maintained. The gaseous effluent consists of a mixture of HCN, ammonia, and water vapor. The crude product mixture flows through an ammonia absorption column where the ammonia is removed by an ammonium phosphate solution. (Dilute sulfuric acid or ammonium sulfate may also be used.) The product stream (mostly gaseous HCN) passes to the product recovery section where it is absorbed in water, distilled, and treated with sulfur dioxide as an inhibitor to prevent polymerization. The ammonium phosphate solution is first stripped of HCN,

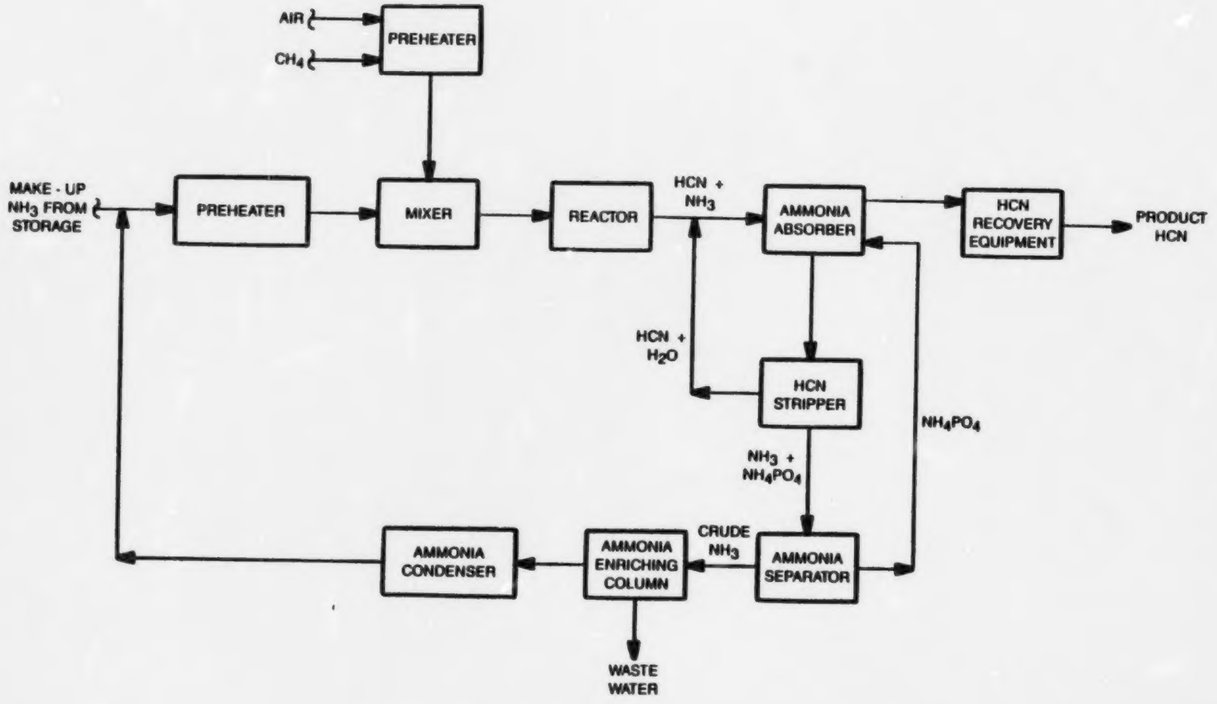

AIR
CH$_4$
PREHEATER
MAKE - UP NH$_3$ FROM STORAGE
PREHEATER
MIXER
REACTOR
HCN + NH$_3$
AMMONIA ABSORBER
HCN RECOVERY EQUIPMENT
PRODUCT HCN
HCN + H$_2$O
HCN STRIPPER
NH$_4$PO$_4$
NH$_3$ + NH$_4$PO$_4$
CRUDE NH$_3$
AMMONIA CONDENSER
AMMONIA ENRICHING COLUMN
AMMONIA SEPARATOR
WASTE WATER

Figure 3-10. Conceptual diagram of typical hydrogen cyanide manufacturing process.

after which it passes to the ammonia recovery columns. The recovered ammonia is condensed and recycled as feed to the process.

Hazardous areas of this process with respect to the potential for a large release of ammonia to the atmosphere (other than the ammonia storage and feed systems) include the feed gas mixer, the HCN reactor, and the ammonia recovery columns. Specifically, the following upsets may occur which could lead to equipment failure and the loss of containment of the reactants:

- Loss of feed gas composition or quantity control;
- Overheating of the reactor; and
- Loss of cooling or heating in the ammonia recovery section.

A loss of feed gas composition is hazardous, because a flammable mixture of ammonia and air may form which would be especially hazardous in the presence of methane. In addition to posing an explosion hazard, an incorrect feed composition or quantity could result in overheating of the reactor, creating the potential for reactor failure from thermal fatigue or overpressure. Other possible causes of overheating in the reactor include poor heat distribution within the reactor bed, resulting in hot spots, and overheating the raw materials before they enter the reactor. Hot spot formation within the reactor can result in catalyst breakdown or physical deterioration of the reactor vessel.

Because the ammonia recovery section involves both stripping columns (heat input) and an ammonia condenser (heat removal), a loss of flow control or other failure affecting the heating or cooling medium could potentially result in overheating and/or overpressure of equipment with subsequent equipment failure and loss of containment of the process streams.

3.2.8 The Manufacture of Hydrazine (17,26)

Hydrazine is produced by the partial oxidation of ammonia with chlorine, hypochlorite, or hydrogen peroxide. Its many uses result from a variety of advantageous properties. It has a high heat of combustion (hence, its use as rocket fuel), is a strong reducing agent, an oxidizing agent under suitable conditions, and a good complexing ligand. However, hydrazine is also a highly reactive chemical and great care must be taken in its manufacture, handling, and storage.

Although there are several processes for the manufacture of hydrazine, the predominant method is based on the oxidation of ammonia with alkaline hypochlorite. A typical flow diagram for this process is presented in Figure 3-11. Liquid chlorine is first absorbed in dilute sodium hydroxide to form sodium hypochlorite. This chemical is then mixed with about a threefold excess of aqueous ammonia to produce chloramine; the reaction is almost instantaneous at a temperature of about 40 °F. Next, a 20-30 molar excess of anhydrous ammonia under pressure is added to the process stream, and the heat of dilution raises the temperature to about 266 °F. The reactor effluent contains hydrazine, ammonia, ammonium chloride, sodium chloride, water, and nitrogen. The nitrogen is scrubbed with water to remove ammonia and is then used as an inert pad to prevent decomposition of hydrazine during the concentration steps. The liquid effluent is preheated and sent to the ammonia recovery section, which consists of two columns. In the first column, ammonia is taken overhead under pressure and recycled to the anhydrous ammonia storage tank. In the second column, some water and final traces of ammonia are removed overhead. The bottom stream from this column, consisting of water, sodium chloride, and hydrazine, is sent on to the hydrazine recovery portion of the process.

Ammonia release hazards are present in this process, because ammonia is recovered in relatively pure form and the product is hydrazine which is not easily handled because of its highly corrosive nature and its hazardous reactivity. For the latter two reasons, hydrazine process equipment is

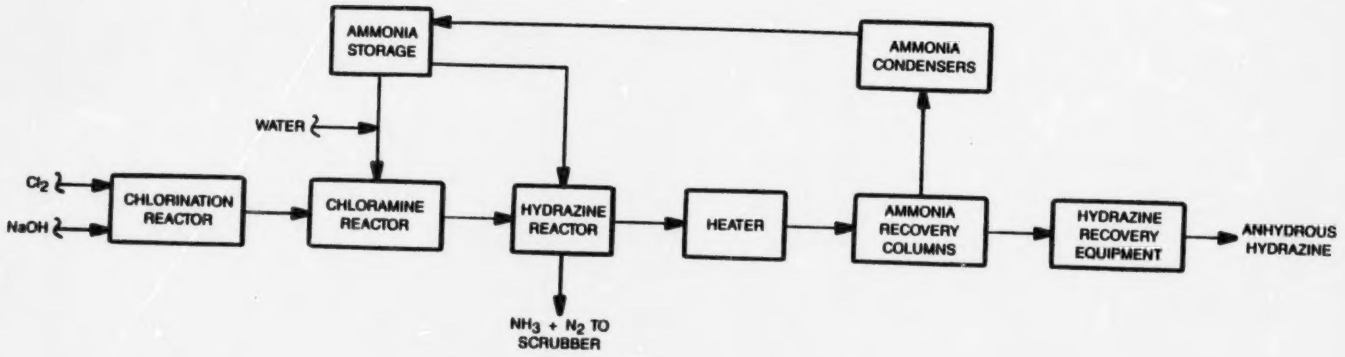

AMMONIA STORAGE
AMMONIA CONDENSERS
WATER
Cl_2
NaOH
CHLORINATION REACTOR
CHLORAMINE REACTOR
HYDRAZINE REACTOR
HEATER
AMMONIA RECOVERY COLUMNS
HYDRAZINE RECOVERY EQUIPMENT
ANHYDROUS HYDRAZINE
$NH_3 + N_2$ TO SCRUBBER

Figure 3-11. Conceptual diagram of typical hydrazine manufacturing process.

stainless steel, and all vessels containing high concentrations of hydrazine in solution are blanketed with nitrogen to prevent ignition. Ammonia release hazards in the ammonia recovery section are a loss of cooling to the ammonia condenser, or overheating of the recovery columns. Both of these failures could lead to dangerous overheating and/or overpressure of equipment.

3.3 REPACKAGING OF ANHYDROUS AMMONIA (27)

In addition to its use in various chemical processes, anhydrous ammonia is also repackaged for resale and further use. Repackaging involves a number of procedures, the use of which depends on whether the liquid ammonia is being transferred from tank cars into tank trucks, or from tank cars, trucks, or bulk storage into cylinders or other portable containers.

Filling operations may be carried out by transferring ammonia directly from the tank car or truck to the receiving container. However, since demurrage begins to accrue after a short period of time, most repackagers first transfer the ammonia to bulk (pressurized) storage before filling the smaller containers. Filling can be accomplished with a compressor or vapor pump by reducing the pressure within the container being filled and at the same time increasing the pressure within the storage tank being emptied. Filling can also be accomplished with the use of a liquid pump. Compressed air should never be used to cause a flow of liquid ammonia, because oxygen contamination in a storage vessel causes stress corrosion cracking in certain carbon steels. During the filling operation the receiving vessels are mounted on scales to determine when they have been filled with the correct amount of ammonia. Some repackagers reweigh the vessels on a second scale to verify that the measurements made with the first scale were accurate.

Potential hazards in repackaging operations include the following:

- Contamination, such as with oxygen (latent hazard);
- Overpressurization of the storage vessel; and

- Overfilling of the receiving vessel.

Stress corrosion cracking of certain carbon steels is caused by oxygen contamination. This hazard is discussed in more detail in Section 3.4. Contamination with other materials could result in potentially violent reactions. Accidental overpressure of the storage tank could result in a release of ammonia from the pressure relief valve if it is not vented to a closed system. Overfilling could cause a release from a rupture in the piping or the receiving vessel from a pressure buildup. A latent hazard also exists in an overfilled vessel which goes undetected and leaves the repackaging facility.

Equipment used in repackaging operations should be constructed from materials compatible with ammonia. Suitable materials of construction for ammonia service are discussed in Section 5. Other potential causes of a release include leaks in the connecting piping as a result of corrosion or loose joint-pipe connections, cloggings of vapor or liquid pipes leading to overpressure, and human error.

3.4 STORAGE AND TRANSFER

All industries which use or handle ammonia in bulk quantities must have appropriate facilities and procedures for the safe storage and transfer of this material. In this section, the potential hazards associated with the storage and transfer of anhydrous ammonia common to all installations are identified. Proper procedures and safety precautions for the control of these hazards for release prevention are discussed in Section 5.

3.4.1 Storage

Liquid anhydrous ammonia is stored in either refrigerated vessels at atmospheric pressure or in pressure vessels at ambient temperatures. The type of vessel used at a particular installation generally depends on the relative costs of the two systems. However, materials and fabrication constraints place an upper limit on the size of pressure vessels, such that no more than 50,000 gallons of ammonia should be stored in an unrefrigerated tank (3). The maximum amount of ammonia that may be stored in a particular vessel, the "filling density", depends on the type of container and ranges from 0.56 to 0.58 times the water weight capacity of the container at 60 °F (7).

Refrigerated Storage--

The predominant use of ammonia in the fertilizer industry has made refrigerated storage economically attractive to producers. This is because the fertilizer season is relatively short, and large single-train plants which produce ammonia year-round require large storage terminals during the off season. The quantities of ammonia involved make pressurized storage prohibitively expensive.

Normally, flat-bottomed, insulated, cylindrical tanks are used for refrigerated storage of anhydrous ammonia at atmospheric pressure. In general, these storage tanks have design pressures of less than 15 psig and are constructed in accordance with Appendix R of the American Petroleum Institute (API) Standard 620 (28). Because of the toxicity of ammonia, however, this standard is considered as a minimum requirement, and many installations are designed to meet stricter standards. Although refrigerated tanks are insulated, heat is still added to the system from the surroundings, and thus vapor is continually generated within the tank. It is therefore necessary to collect, reliquify, and return the vapor to the tank. A closed vapor return system is necessary, not only to prevent the release of ammonia to the atmosphere but also to prevent contamination of the stored ammonia with oxygen. A typical refrigerated storage system is shown schematically in Figure 3-12. The system in this figure extracts unwanted heat from the stored liquid by drawing low-pressure ammonia vapor from the tank, compressing it, and delivering it at a sufficiently high pressure for the condenser cooling medium to reliquify it.

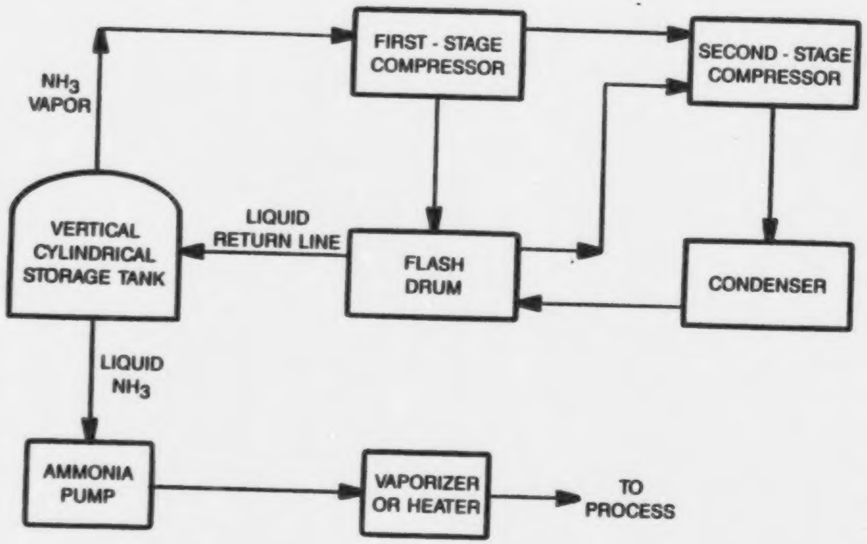

FIRST - STAGE COMPRESSOR
SECOND - STAGE COMPRESSOR
NH$_3$ VAPOR
LIQUID RETURN LINE
VERTICAL CYLINDRICAL STORAGE TANK
FLASH DRUM
CONDENSER
LIQUID NH$_3$
AMMONIA PUMP
VAPORIZER OR HEATER
TO PROCESS

Figure 3-12. Conceptual diagram of typical atmospheric refrigerated ammonia storage system.

There are basically two types of refrigerated storage tanks, single- and double-wall. A single-wall tank consists of a single shell with a domed roof. The roof and side walls are clad with insulation; the materials usually used for insulating single-wall tanks are foamed polyurethane or polyisocyanurate, expanded polystyrene, and foamed glass (17). These materials all require a vapor seal over the entire outer surface in order to prevent moisture from entering the insulation or the space between the insulation and the tank. A double-wall tank consists of an inner tank designed to store ammonia under the required conditions, surrounded by a carbon steel outer tank. The gap between the shells is usually not less than 18" and is filled with a powdered insulant (Perlite) or wool fiber. A third type of tank is sometimes used which is a variation of the double-wall tank. This type of tank is called a "double-integrity" system whereby the outer shell is designed to hold all of the liquid in the event of a total failure of the main tank.

Regardless of the type, all storage tanks must be supported on suitable foundations with a layer of load-bearing insulation placed between the tank bottom and the base. With certain foundation designs, it is also necessary to install a foundation heating system to prevent the temperature of the subgrade from falling below 32 °F. This is because the continuous formation of ice lenses on some soils will cause the ground to heave (commonly referred to as "frost heave") with the resultant risk of damage to the underside of the tank.

Pressurized Storage--

In general, pressurized storage containers are used in conjunction with processes which require relatively small quantities of ammonia (less than 40,000 gallons stored). Pressurized storage tanks are generally constructed of carbon steel according to the American Society of Mechanical Engineers (ASME) Code for Unfired Pressure Vessels, Section VIII, Division I, and with the American National Standards Institute (ANSI) Standards for Piping and Fittings (29,30,31,32). Stationary pressurized storage vessels are usually cylindrical in shape with formed ends and may be installed with the axis either vertical or horizontal. Transportable cylinders are a special type of pressurized storage which are used when only small quantities (usually no more than 150 lbs) of ammonia are required.

Storage System Hazards--

A large release of anhydrous ammonia from a refrigerated or pressurized storage system would result from failure of the storage vessel or its associated piping. The failure might occur as a result of over- or underpressure of the vessel, or as a result of weakened areas of the vessel walls which ruptured as a result of a very small applied stress. Possible causes of vessel failure include the following:

- Improper materials of construction,
- Corrosion,
- Overheating,
- Overfilling,
- External damage, and
- Failure of safety relief devices.

The importance of using the proper materials of construction for ammonia storage, especially refrigerated systems, cannot be overstressed. Refrigerated storage equipment is frequently subjected to subzero temperatures which may be as low as -28 °F. The significant difference between vessels working at ambient temperature and refrigeration temperatures of this order is that carbon steel vessels working at subzero temperatures are more liable to brittle fracture under stress. The "transition temperature" for various casts and types of steel ranges from -58 °F to 50 °F (17). For brittle fracture to occur, the steel must be below its transition temperature, there must be a notch or crack generally in association with a weld, and there must be sufficient stress to cause plastic strain in the region where the stress is concentrated by the notch. Once a fracture is initiated at the notch, it may propagate at high speed under the influence of quite low applied stresses.

A predominant internal corrosion hazard of ammonia storage tanks is stress corrosion cracking (SCC) which occurs in certain carbon steels and has been the subject of extensive research over the last thirty years. The effects of SCC are several hundred or more fine cracks invisible to the naked eye which vary in depth from less than a millimeter to the full thickness of the plate (17). The cracks always occur in zones of high stress, usually the weld deposit. Cracking susceptibility increases with the strength of the steel and with temperature. It is generally agreed that the primary cause of SCC is contamination with oxygen; it is postulated that cracking may be induced in some vessels with an oxygen concentration as low as 1 ppm (33). The addition of 0.1 to 0.2 wt% of water has been found to inhibit cracking in the liquid phase, but this practice does not prevent cracking in the vapor phase (34). No SCC has been reported in refrigerated storage vessels; it is assumed that the reason for this is that any oxygen present is removed in the recompression cycle and not because of the low temperature and pressure (33). As pressurized vessels are often associated with frequent transfer operations, contamination of the ammonia with air is a definite risk. If prompt detection of SCC is not made, a serious corrosion hazard exists which may ultimately lead to complete failure of the vessel.

In addition to stress corrosion cracking, an external corrosion hazard exists if storage vessels are in constant contact with dampness or standing water. Furthermore, if corrosive materials are stored near ammonia storage vessels, fugitive emissions of these materials would enhance the possibility of external corrosion of an ammonia storage tank.

An uninsulated storage vessel filled with ammonia at the maximum filling density will become liquid full at a temperature of 130 °F (7). Thus, an overheating hazard exists if ammonia is stored in an area which is located near flammable or incompatible materials, especially if the area is not well ventilated or heavily trafficked, or if storage vessels are exposed to direct sunlight. An overheating hazard exists in refrigerated storage systems because of the dependence on the components of the refrigeration system to maintain the low temperature of the system by removing and recompressing the vapor phase. If this system were to fail, the temperature in the vessel would increase, and the pressure would eventually exceed the design pressure of the vessel.

Overfilling of storage vessels may occur as a result of a malfunctioning scale, level gaging device or operator error. An overfilled ammonia storage tank presents a hazard, because the temperature at which the vessel will become liquid full is lowered. This creates the possibility of a liquid full container with an otherwise insignificant increase in temperature. The resulting hydrostatic pressure would cause the pressure relief device to vent ammonia to the atmosphere; if the pressure relief device failed to activate, a catastrophic release could result from vessel rupture.

Single-wall refrigerated storage vessels are especially vulnerable to external damage due to the ingress of moisture which will subsequently freeze and damage the installation. Poor vapor sealing, which allows moisture to enter the insulation or the space between the insulation and the tank, is often directly responsible for insulation failures (17). Another potential cause of external damage is failure of the tank base heating system with the subsequent formation of ice on the subgrade, resulting in "frost heave" which was discussed previously. Insulation or other forms of external damage may also result from high winds or other severe weather conditions. Hence, storage vessels located in regions with a high frequency of violent storms, earthquakes, or high winds present a greater risk of external vessel damage than those located in areas with mild weather conditions.

In the event of an overpressure of a storage vessel, the safety relief valve(s) would open, allowing the pressure to be relieved by venting ammonia to the atmosphere. Likewise, if a partial vacuum were to occur in a refrigerated storage vessel, the vacuum relief valves would open and allow material (such as air) from the discharge side of the relief valve to enter the vessel. If the relief valve in either of these situations failed to open, the structural design conditions of the tank could be exceeded, potentially resulting in the catastrophic failure of the container.

3.4.2 Transfer from Tank Cars and Trucks

Appropriate procedures must be followed when transferring ammonia from tank cars and trucks to storage vessels to reduce the risk of a hazardous chemical release. Tank cars are generally unloaded by using a gas compressor or transfer unit to create a pressure differential between the storage vessel and the tank car. Tank cars may also be unloaded with the use of a liquid pump (1,7). Examples of hazards associated with the unloading of tank cars and trucks include the following:

- The pressure in the tank car or truck attains the pressure setting of its relief valve, and ammonia vapor is vented to the atmosphere;

- The pressure in the tank car is lowered to the extent that the tank is subjected to an internal vacuum condition, possibly caused by a subsequent reduction of ambient temperature;

- The vapor or liquid transfer line becomes clogged or control valve fails in the closed position resulting in an overpressure of the storage vessel;

- Leakage resulting from pipe corrosion or poor pipe-joint connections;

- Incompatible contamination in the receiving vessel which could result in an uncontrolled reaction with overpressure, or corrosion of the receiving vessel;
- A malfunctioning level indicating device on the receiving vessel resulting in an overflow of the receiving vessel; and
- Human error.

3.4.3 Transfer from Storage Vessels

Another aspect of the transfer of liquid or vapor ammonia is its transfer from a storage container to its designated use in the plant. This is generally accomplished with the pressure differential between the container and the receiving vessel or process to which it is flowing.

One hazardous transfer practice is manifolding to withdraw liquid ammonia from two or more cylinders simultaneously. This is because under certain temperature conditions it is possible for liquid to flow from one cylinder into another cylinder until it is completely filled (1). If the valve of this completely filled cylinder were subsequently closed, any rise in temperature would result in a build-up of hydrostatic pressure and could result in the rupture of the cylinder. Because evaporation within a cylinder may cause the ammonia to be refrigerated to a point where there is little or no flow of ammonia vapor to a process, cylinders are often manifolded together to increase the total vapor withdrawal rate. Gaseous transfer between cylinders at different temperatures in such an arrangement is likewise potentially hazardous if there is subsequent reliquefaction and isolation of an overfilled container.

Nitrogen or air padding should never be used to promote the flow of ammonia from cylinders or other storage vessels. Hazards include dangerous high pressures as a result of an increase in the ambient temperature and oxygen contamination which causes stress corrosion cracking. Furthermore, a cylinder should never be warmed with a flame to increase the vapor discharge rate because of possible pressure buildup sufficient to rupture the container. Warming by other methods such as a water bath should be done with caution so as to prevent accidental overpressure of the cylinder.

Other transfer hazards include:

- Potential backflow of foreign material into the cylinder or into the upper valve chambers of the ammonia storage vessel;
- Isolation of liquid ammonia in piping between closed valves which could lead to bursting of the line from a build-up in hydrostatic pressure with a temperature increase; and
- Failure of piping connections from corrosion, improper materials of construction, or work hardening or fatigue.

3.4.4 Transporting Ammonia Storage Containers

Unloading containers of ammonia from the delivery vehicle or moving them within the plant is another aspect of the storage and transfer of this material. In general, hazards associated with the transport of ammonia within a closed vessel arise from failure to follow the proper transport procedures in a safe manner. Prevention of a hazardous release resulting from human error is discussed in Section 5.6.

SECTION 4

POTENTIAL CAUSES OF RELEASES

The potential for a hazardous release of liquid or gaseous ammonia exists in any type of facility which handles this material. The possible sources of such a release are numerous. Large amounts of ammonia may be released from leaks or ruptures of large storage vessels (including tank cars on-site) or failure of process machinery (e.g., pumps or compressors) which maintain a large throughput of ammonia gas or liquid. Smaller releases may occur as a result of ruptured lines, broken gauge glasses, or leaking valves, fittings, flanges, valve packing, or gaskets.

In Section 3, specific release hazards associated with the manufacture, consumption, and storage of anhydrous ammonia were identified. In addition to those discussed in the preceding section, there are also numerous general hazards which, if realized, could lead to an accidental release. Both specific and general hazards in ammonia facilities may be broadly classified as process, equipment, or operational causes. This classification is for convenience only. Causes discussed below are intended to be illustrative, not exhaustive. More detailed discussions of possible causes of accidental releases are planned for other parts of the prevention reference manual series.

4.1 PROCESS CAUSES

Process causes are related to the fundamentals of process chemistry, control, and general operation. Possible process causes of an ammonia release include:

- Loss of feed composition control resulting in the formation of ammonia-air mixtures within the flammability limits;

- Backflow of process reactants to an ammonia feed tank;
- Excess feeds in any part of a process leading to overfilling or overpressuring equipment or excess feed to a reactor;
- Loss of condenser cooling to distillation units;
- Overheating of reaction vessels and distillation columns; and
- Overpressure in ammonia storage vessels from overheating as a result of fire exposure or unrelieved overfilling.

4.2 EQUIPMENT CAUSES

Equipment causes of accidental releases result from hardware failures. Some possible causes include:

- Failure of feed control systems from a loss of power, clogged lines, jammed valves, or instrument failure;
- Excessive stress on materials of construction due to improper fabrication, construction, or installation;
- Failure of pressure relief systems;
- Mechanical fatigue and shock in any equipment (mechanical fatigue could result from age, vibration, excessive external loadings, or stress cycling; shock could occur from collisions with moving equipment such as cranes or other equipment in process or storage areas);

- Thermal fatigue and shock in reaction vessels, heat exchangers, and distillation columns;

- Equipment constructed of high alloys, especially high strength alloys selected to reduce the weight of major process equipment, which might be especially sensitive to corrosion or severe operating conditions;

- Brittle fracture in low temperature equipment subjected to large temperature swings or creep failure which might occur in equipment previously subjected to a fire that may have caused undetected damage; and

- All forms of corrosion including stress corrosion cracking from oxygen contamination, pipe connections which have slowly corroded as a result of contaminants entering the system when cylinders are switched, and external corrosion from exposure to precipitation or constant dampness.

4.3 OPERATIONAL CAUSES

Operational causes of accidental releases are a result of incorrect procedures or human errors. These causes include:

- Overfilled storage vessels;

- Improper process control system operation;

- Errors in loading and unloading procedures;

- Poor quality control resulting in replacement parts which do not meet system specifications;

- Inadequate maintenance in general, but especially on pressure relief systems and other preventive and protective devices; and

- Lack of inspection and non-destructive testing of vessels and piping to detect corrosion weakening.

SECTION 5
HAZARDS PREVENTION AND CONTROL

5.1 GENERAL CONSIDERATIONS

Prevention of accidental releases relies on a combination of technological, administrative, and operational practices. These practices apply to the design, construction, and operation of facilities where ammonia is stored and used. When developing a thorough release prevention and control plan, considerations must be made in the following areas:

- Process design,
- Physical plant design,
- Operating and maintenance practices, and
- Protective systems.

In each of these areas, consideration must be given to specific factors that could lead to a process upset or failure which could directly or indirectly cause a hazardous release of ammonia to the environment. At a minimum, equipment and procedures should be examined to ensure that they are in accordance with applicable codes, standards, and regulations. Further evaluations should then be made to determine where extra protection against a release is appropriate so that stricter equipment and procedural specifications may be developed.

The following subsections discuss specific considerations regarding release prevention; more detailed discussions may be found in a manual on control technologies, part of this manual series.

5.2 PROCESS DESIGN

Process design considerations involve the fundamental characteristics of the processes which use ammonia. These considerations include an evaluation of how deviations from expected process design conditions might initiate a series of events that could result in an accidental release. The primary focus is on how the process is controlled in terms of the basic process chemistry and the variables of flow, pressure, temperature, composition, and quantity. Specific considerations may include mixing systems, fire protection, and process control instrumentation. Modifications to enhance process integrity may result from review of these factors and might involve changes in quantities of materials, process pressure and temperature conditions, the unit operations, sequence of operations, the process control strategies, and instrumentation used.

Table 5-1 shows the relationship between some specific process design considerations and individual processes described in Section 3 of this manual. This does not mean that other factors should be ignored, nor does it mean that proper attention to just the considerations in the table ensures a safe system. The considerations listed, and perhaps others, must be properly addressed if a system is to be safe, however.

The most significant considerations are aimed at preventing overheating and/or overpressurizing systems containing ammonia. Overheating is hazardous because it may lead to overpressure which weakens process equipment and adds to the potential for leaks at joints and valves. Wide temperature fluctuations also significantly decrease the lifespan of many materials of construction. Overpressure may occur without overheating if flowrate control of both gas and liquid streams is not maintained.

5.3 PHYSICAL PLANT DESIGN

Physical plant design considerations include equipment, siting and layout, and transfer/transport facilities. Vessels, piping and valves, process machinery, instrumentation, and factors such as location of systems

TABLE 5-1. SOME PROCESS DESIGN CONSIDERATIONS FOR PROCESSES INVOLVING ANHYDROUS AMMONIA

Process Design Consideration	Process or Unit Operation
Contamination (with air especially)	Feed systems, storage tanks, SCR catalyst
Flow control of ammonia feed	All
Temperature sensing and heating medium flow control	Distillation and stripping column reboilers, feed preheaters, reactors
Temperature sensing and cooling medium flow control	Distillation and stripping column condensers, reactors
Adequate pressure relief	Storage tanks, reactors, refrigeration condensers, distillation and stripping columns, heat exchangers
Corrosion monitoring	Pressurized storage tanks, neutralization equipment
Temperature monitoring	Distillation and stripping column reboilers, storage tanks, catalytic converters
Level sensing and control	Storage tanks, reboilers and condensers

and equipment must all be considered. The following subsections discuss specific design aspects of facilities which handle anhydrous ammonia.

5.3.1 Equipment

The design of equipment for anhydrous ammonia calls for special and up-to-date knowledge, particularly where low-temperature conditions are encountered. The following paragraphs are intended to familiarize the reader with the kinds of equipment which are used in ammonia service with specific reference to materials of construction, safety devices, and safe operation. The discussions herein are not intended as specifications; the appropriate standards should be consulted and expert advice should always be sought in the design and procurement of equipment for liquid ammonia duty.

Materials of Construction--

Dry ammonia is noncorrosive to most common metals. However, moist ammonia corrodes copper, tin, zinc, and many alloys, particularly copper alloys. Therefore, only iron or steel, despite the fact they decrease the minimum ignition temperature, or other nonreactive material should be used in contact with ammonia (8).

Carbon and carbon-manganese steels are commonly used for various types of equipment in ammonia service. As discussed in Section 3.4.1, one of the primary concerns with ammonia storage is the susceptibility of certain carbon steels to stress corrosion cracking in the presence of small amounts of oxygen contamination. Although it is not possible to specify a particular type of carbon or carbon-manganese steel which will definitely not succumb to stress corrosion cracking, it has been found that low-strength steels (yield less than 350 N/mm^2) are less susceptible to cracking than high-strength steels, and thermal stress relief seems to completely eliminate the mechanism (17).

Piping for ammonia service should be constructed of rigid steel (11). Copper, brass or galvanized fittings should not be used. Unions, valves, gauges, pressure regulators and relief devices having copper, brass or bronze parts are not suitable for ammonia service. Certain aluminum alloys may be used for various components in ammonia systems. Mercury thermometers in ammonia service should be avoided (3).

Metallic and nonmetallic gasket materials, such as compressed asbestos, graphited asbestos, carbon steel or stainless steel spiral-wound asbestos filled, and aluminum are suitable for ammonia service. Perfluorinated plastic materials and neoprene have also been found suitable if they are fully confined so as to prevent creep or blow out in the event of elevated temperatures (1).

Storage Vessels--

A large inventory of ammonia contained in storage vessels on site represents one of the most hazardous components of a facility which uses or produces this material. This fact has manifested itself in the number of accidental releases from storage tanks over the years. In this section, the different types of ammonia storage vessels are briefly discussed along with the associated protection devices and safety procedures which are designed for the prevention of a hazardous release of this material. For detailed specifications of ammonia storage systems the reader is advised to consult references (1) and (7).

Anhydrous liquid ammonia is stored commercially at full pressure, partially refrigerated, and fully refrigerated in vessels ranging from two pound cylinders to multi-ton tanks. In general, the quantity of ammonia determines the choice of container, which in turn influences the maximum storage pressure. Storage at ambient temperature (full pressure) is restricted to relatively small vessels, usually uninsulated and cylindrical in shape with rounded ends. The most frequent sizes range from 500 to 45,000 gallons (1). These containers must be designed for pressures of at least 250 psig and constructed in accordance with the American Society of Mechanical Engineers (ASME), Boiler and Pressure Vessel Code, Section VIII, Division 1 (29). If the pressure is only partially reduced, the vessel is usually spherical in shape and insulated. The pressure in a "semi-pressure" storage vessel is selected to suit the individual requirements of the site process. This type of storage is not as prevalent today as in the past due to the increasing amount of ammonia which is being stored and transported in the fully refrigerated state.

Full refrigeration of the liquified gas at -27.4 °F reduces the pressure essentially to atmospheric. However, a slight positive pressure is necessary to accommodate minor pressure fluctuations and to avoid negative pressure on the tank, since air must be excluded. Normally, refrigerated vessels are flat-bottomed, insulated, cylindrical tanks which are mounted vertically. Tanks with design pressures of 15 psig or less should be constructed in accordance with American Petroleum Institute (API) Standard 620 (28) as a minimum, while those with higher design pressure should conform to the ASME Code cited above.

The most probable causes of failure of an ammonia storage vessel were discussed in Section 3.4 and include corrosion and the buildup of hydrostatic pressure in a liquid-full container caused by overfilling or overheating. Other possible causes of storage tank failure include brittle fracture from overstressing, the use of improper materials of construction, and external damage. This section discusses the safety devices and precautions designed to minimize the chances of an accidental release as a result of one of these causes.

Precautions should be taken to prevent both internal and external corrosion of ammonia storage vessels. Stress corrosion cracking in ammonia storage vessels is caused by the contamination of the ammonia with air (oxygen). The primary means of preventing this type of corrosion is by the addition of at least 0.2% water. This is not an absolute safeguard, however, because cracking can still occur in the areas of the vessel which are exposed to the vapor phase. Preventive measures which may be taken to reduce the risk of stress corrosion cracking include the following (33):

- Reduce the tensile stress by thermal stress relief of the entire vessel;

- Decrease the residual welding stresses by shotpeening or stress relieving crown plates, leg column plates, and bottom plates in a furnace prior to commissioning;

- Careful purging when commissioning; and

- Purge the vapor space with an oxygen free inert gas on a regular basis.

Prevention of external corrosion involves good housekeeping and maintenance practices which assure that containers are never in contact with standing water or exposed to continual dampness.

Brittle fracture of steel is another potential cause of vessel failure. It generally occurs in the vicinity of a notch or crack when the material is below its transition temperature. To lower the susceptibility of carbon steel to brittle fracture, vessels should either be built of a steel having a transition temperature not higher than the design temperature, or steps should be taken to eliminate plastic strain of the notches, since it is not possible to be certain that all surface imperfections have been eliminated (17). This may be achieved by thermal stress relieving the vessel after fabrication.

Pressure relief valves and rupture discs are designed to allow a controlled release of overpressurized contents. According to American National Standard (ANSI) K61.1, ammonia storage containers (with the exception of small cylinders) should be provided with one or more pressure relief valves of the spring-loaded type which are set to discharge at a pressure not exceeding the design pressure of the container. The Compressed Gas Association (CGA) specifies that the maximum discharge rate of the valve should be such that the pressure in the container will not exceed 120% of the design pressure (1).

Further provisions recommended by the CGA and ANSI K61.1 include the following (1,7):

- The discharge from pressure relief valves should be directed away from the container upward and unobstructed to the open air.

- Vent pipes should not be restrictive nor smaller in size than the pressure relief valve outlet connection.

- Vent pipes should have loose-fitting caps to exclude water and debris but not restrict free discharge of vapor. In addition, suitable provision should be made for draining condensate which may accumulate.

- Shut-off valves should not be installed between the pressure relief valves and the container unless the arrangement is such that full flow is possible through at least one nonisolated pressure relief valve at the required capacity. (Dual relief valves are usually fitted which can be isolated individually and are interlocked so that a relief valve can be removed for servicing without losing protection of the vessel (17).)

Furthermore, it is important to ensure that if the relief valve lifts, the ammonia vapor can be vented harmlessly. This may mean leading the vent to a stack, the height and position of which is related to work areas in the vicinity.

A cylinder containing less than 165 pounds of ammonia is not required to have a pressure relief device (1). Instead, cylinders are designed to withstand very high pressures, as these containers are generally used indoors where product containment is paramount. Regardless of the higher design pressure, these containers should be protected from fire and direct exposure to the sun, because they are still susceptible to becoming liquid-full from an increase in temperature. Without a pressure relief device, overpressure would result in a sudden rupture and complete discharge of the cylinder contents.

Protection from overheating of larger pressurized storage vessels may be provided by a shield to prevent direct exposure to the sun and by painting the vessel with some reflective paint.

Atmospheric and semipressure storage tanks should be equipped with instrumentation to ensure that the design pressure is not exceeded. This is often done by having a pressure controller which will stop and start the refrigeration system as required to maintain tank pressure. Provision should also be made to reduce or stop any incoming ammonia once the refrigeration system is fully loaded. In the event of a total failure of the refrigeration plant, the pressure in the storage vessel will rise until it reaches the design pressure of the relief valve, at which time it will begin to vent to the atmosphere. Therefore, a standby diesel generator should be provided in case it is not possible to restore the power before the design pressure of the relief valve is attained.

Refrigerated storage vessels operating at atmospheric pressure, in addition to having relief valves for overpressure, must also be protected from underpressure, since these vessels can only withstand a few inches water gauge of vacuum. Negative pressure (vacuum) relief valves are therefore provided which allow warm ammonia gas to flow from the refrigeration system back into the vessel in the event that pressures below atmospheric develop in the vessel.

In addition to venting provisions, storage vessels should have valve arrangements which allow the vessel to be isolated from the process to which the ammonia is being fed. Backflow of material into the upper valve chambers when the feed valve is shut off at the storage tank must be prevented because of the possibility of corrosion in the feed pipe. Other valve specifications found in ANSI K61.1 require storage tank filling connections to be provided with an approved combination back-pressure check valve and excess flow valve; one double or two single back-pressure check valves; or a positive shut-off valve, in conjunction with either an internal back-pressure valve or an internal excess flow valve (7). Each container should also be equipped with a vapor return valve. Furthermore, it is good practice to place a valve in the liquid outlet pipe as close to the tank as possible which is capable of remote closure in the event of a pipe failure during a transfer operation.

To reduce the risk of overfilling during transfer operations, smaller storage vessels are often mounted on a scale which will indicate the weight of fluid in the container at all times. All bulk storage vessels should also be equipped with a reliable liquid level gauge which allows for quick and accurate readings. The design and installation of an ammonia liquid level gauge should adhere to the requirements given in ANSI K61.1 (7). Most ammonia storage tanks have float-type gauges whereby a float mechanism is magnetically coupled to a pointer which indicates percent of capacity on a volume basis (1). Although this is an accurate method of measuring the level, the equipment is vulnerable to mechanical damage and is often supplemented with an additional measuring device. A differential pressure gauge which measures the static head of the liquid is one possible back-up (17). Each nonrefrigerated storage container nameplate should include markings which indicate the maximum level to which the container may be filled with liquid ammonia between 20 °F and 100 °F. The percent of the maximum volume of the container which may be filled with liquid ammonia for various temperatures is given in Table 5-2. Because refrigerated, atmospheric storage tanks are maintained at a fairly constant temperature, they may be filled to within a few inches of the roof/wall seam.

As an overfilled storage vessel is a serious hazard, it is normal for level indicators to be fitted with high-level alarms to warn the operator when the maximum filling level has been reached (17). Important level alarms should be connected to the vessel separately from the level controller in case

TABLE 5-2. MAXIMUM SAFE VOLUME OF LIQUID AMMONIA IN NONREFRIGERATED STORAGE CONTAINERS AT VARIOUS TEMPERATURES (1)

Temperature of Liquid Ammonia in Tank °F	Maximum Safe Volume Liquid Ammonia as a % of Container Water Volume
30	87.3
40	88.3
50	89.5
60	90.7
70	91.8
80	93.0
90	94.4
100	95.7

the bottom lead line of the level controller inadvertently becomes blocked by oil and/or dirt. As a further precaution, a short, vented dip pipe can provide protection from overfilling in the event of failure of the volume or weight measuring device. However, this device will not prevent an overflow of ammonia liquid. Furthermore, it will only work if there is no other outlet from the vapor space and if the line to the vent system has enough capacity. It is therefore recommended that a vessel be fitted with a relief device which discharges to an overflow tank or other suitable receiver if the possibility of overfilling exists.

Process and Reaction Vessels--

General considerations for hazard control for storage vessels also apply to the design and use of process and reaction vessels. In the latter type of vessels, however, there is a greater degree of risk, as these containers are often exposed to more severe conditions of temperature and/or pressure than a regular storage vessel.

Primary considerations for process and reaction vessels include:

- Materials of construction,
- Pressure relief devices,
- Temperature control,
- Overflow protection (in addition to high level alarms), and
- Foundations and supports.

The foundations and supports for vessels are important design considerations, especially for large storage vessels and tall equipment such as distillation columns. The choice of construction materials is also an important consideration particularly where low-temperature conditions are encountered.

Expert advice should always be sought in the design and procurement of equipment for liquid ammonia duty.

If cooling to a condenser is lost, overpressure may occur. Thus, it is necessary to use pressure relief valves to protect against leaks and ruptures which can result from overpressure. Pressure relief protection is also necessary in the event of a fire.

Distillation and stripping columns present significant release hazards because they may contain large amounts of ammonia in pure form and have a heat input. As they are often located outdoors, external factors such as ambient temperature fluctuations and wind loadings must be properly accounted for in their design and consttuction, especially for the support structure.

Piping-

All ammonia piping should be extra heavy (schedule 80) steel when threaded joints are used (1). However, schedule 40 piping may be used when joints are either welded or joined by flanges. All refrigeration system piping should conform to ANSI B31.5 - American National Standard for Refrigeration Piping (35). Iron and steel piping, fittings, and valves are suitable for ammonia gas and liquid. Nonmalleable metals, such as cast iron, must not be used for fittings (1). As low temperature embrittlement is a concern in ammonia systems, material selection must take this into account. In general, if a material is not notch-tough at the operating temperature, the welds should be subjected to post-weld heat treatment.

Because liquid NH_3 expands with temperature, bursting of lines due to hydrostatic pressure must be prevented. This may be accomplished with expansion chambers which should be located at the highest point of each section that may be closed, trapping liquid NH_3. Construction of these chambers should be in accordance with the ASME Code for Unfired Pressure Vessels, Section VIII (29). An expansion chamber device typically consists of a rupture disk and a receiver chamber which can hold 20-30% of the protected line's capacity. The chamber is equipped with a pressure indicator or alarm switch set to function upon disk rupture. Alternatively, a hydrostatic relief valve may be installed in each section of piping in which liquid ammonia can be isolated between shut-off valves.

The following is a list of general guidelines for the safe transport of liquid ammonia in piping systems:

- Piping systems should have as simple a design as possible with a minimum number of joints and connections; flow should not be restricted by an excessive number of elbows and bends.
- Piping should be at least 7.5 feet above the floor if possible; provision should be made to protect all exposed piping from physical damage that might result from moving machinery, the presence of automobiles or trucks, or any other undue strain that may be placed on the piping.
- In addition to being securely supported, pipes should be sloped with drainage provisions at the low points.
- Clips or hangers should not fit too tightly to allow for thermal expansion of the pipe.
- Piping should be protected from exposure to fire and high temperatures.
- A pressure reducing regulator should be installed when connecting to lower pressure piping or systems from storage vessels.

- Low points should be avoided in inlet lines to relief valves for ammonia vapors, because liquid can condense in these lines under ambient conditions.

- Pipelines should always be emptied when ammonia flow is not required to prevent the possible isolation of liquid NH_3 between closed valves.

Valves--

Valves in ammonia service are discussed in a number of references (1,7,24). Several types of valves including gate, globe, ball, and check configurations are used in ammonia systems. Construction may be of iron or steel. Copper and copper-bearing materials must not be used for the valve or trim parts, because these materials are attacked by ammonia (when moisture is present.)

It is good practice to locate stop valves in the inlet and outlet lines to all condensers, vessels, evaporators, and long lengths of pipe so they can be isolated in case of leaks and to facilitate pumping out. If globe-type valves are used they should be installed with the valve stem horizontal to lessen the chance for dirt or scale to lodge on the valve seat or disk (24).

Pressure regulators, solenoid valves, and thermal expansion valves should be flanged for easy assembly and removal. A strainer should be used in front of self-contained control valves to protect them from pipe construction material and dirt (24). Solenoid valves should be located upright and protected from moisture. A manual opening stem is useful for emergencies.

When ammonia flow is shut off at the feed tank, the piping system between that point and the point of application is filled with vapor. Gradual absorption of the vapor in the process fluid leaves a vacuum which draws ammoniated fluid back into the piping system. This may cause serious problems, especially if the shut-off point is upstream from instruments and other items of equipment. A diaphragm-operated check valve held in a closed position by ammonia pressure may be used to prevent undesired back or reverse flows. If the ammonia pressure falls and pressure on the diaphragm becomes subatmospheric, the valve opens and allows air to flow into the piping system, thus breaking the vacuum which would otherwise cause backflow of the process fluid.

Excess flow valves should be considered for ammonia in vessels, tank cars, and other places where unintentional high liquid discharge rates need to be prevented. In the event that a liquid discharge line is broken, the resulting high flow rate would cause the valve to close off, restricting the escape of ammonia.

The pressure of ammonia gas can be controlled by a pressure reducing and regulating valve of steel construction. The valve should be designed for the range of conditions under which it will be required to operate, taking into account the maximum and minimum flow of ammonia gas, its average temperature, and the average upstream and downstream pressures (1).

Process Machinery--

Process machinery refers to rotating or reciprocating equipment that may be used in the transfer or processing of ammonia. Included in this classification are pumps and compressors which may be used to move liquid or gaseous ammonia where gas pressure padding is insufficient or inappropriate.

Pumps-- Any pump used in ammonia service must conform to ANSI/UL 51 - American National Standard for Power-Operated Pumps for Anhydrous Ammonia and LP Gas (36). To assure that a given pump is suitable for an ammonia service application, the design engineer should obtain information from the pump manufacturer certifying that the pump will perform properly in this application.

Centrifugal pumps are normally used for pumping liquefied ammonia in a fully refrigerated condition (17). Glandless, canned type or conventional pumps fitted with either a single mechanical seal together with a soft packed auxiliary gland or a double mechanical seal may be used. Canned pumps are generally used indoors or in congested areas. When a glanded pump is used a mechanical seal is advisable followed by a soft packed gland (17). The seal pressure should not exceed the manufacturer's recommendations, and the interspace should be vented in a safe manner.

Pumps should be constructed with materials which are resistant to ammonia at operating temperatures and pressures. Lubricating oil should be resistant to breakdown as a result of contact with ammonia. In some cases, the potential for seal leakage may rule out the use of rotating shaft seals. Some pump types which either isolate the seals from the process stream or eliminate them altogether include canned motor, vertical extended spindle submersible, magnetically-coupled, and diaphragm (4).

Net positive suction head (NPSH) considerations are especially important for ammonia, since the liquid may be pumped near its boiling point. Long suction lines reduce the effective NPSH available, and if the suction lines are very long in relation to the NPSH available, a vapor release vessel should be fitted in the suction line as close to the pump as possible (17). The pump supply tank should have high and low level alarms, and the pump should be interlocked to shut off at low supply level or low discharge pressure.

Centrifugal pumps often have a recycle loop back to the feed container which prevents overheating in the event that the pump is deadheaded (i.e., the discharge valves close). Positive displacement pumps can be equipped with a constant differential relief valve capable of discharging the entire capacity of the pump into the suction port of the pump to prevent rupture in the event of deadheading. When a positive displacement pump is used to reduce the chance of backflow, such a relief valve could defeat this purpose if the back pressure were high enough. In such a case, the relief valve discharge should be routed somewhere other than the suction part of the pump. Pumps can also be protected by a differential pressure switch fitted across the pump to trip the motor should a low-pressure condition arise. This could be caused by inadequate priming, by vaporizing in the pump, or by too low a suction head.

Compressors-- Ammonia compressors include reciprocating, centrifugal, liquid-ring rotary, and non-lubricated screw compressors. Usually two-stage reciprocating compressors are used for ammonia service, although rotary compressors are also common and may be preferable if it is necessary to avoid oil contamination (17). Detailed descriptions of the different types of compressors may be found in the technical literature (4).

As with pumps, materials of construction must be selected which are compatible with ammonia at the operating conditions. Copper and copper-bearing alloys must be avoided and particular attention paid to the gland arrangement (17). Any ammonia compressor must be designed for at least 250 psig working pressure except those used for refrigeration service.

A pressure relief valve large enough to discharge the full capacity of the compressor should be installed between the discharge of the compressor and the high pressure shut-off valve. If the crank case is not designed to withstand system pressure, it should also be protected with a suitable pressure relief valve. In addition, a liquid trap should be installed before the compressor suction to prevent entry of liquid into the compressor.

Miscellaneous Equipment--

Pressure Relief Devices-- Pressure relief devices for ammonia service should be constructed in accordance with CGA S-1.3 - "Pressure Relief Device Standards - Part 3 - Compressed Gas Storage Containers" (37). All wetted parts of relief valves and rupture disks should be constructed from materials compatible with ammonia at the operating temperature and pressure. For balanced relief valves, the balance seals must also be made of appropriate materials.

Measures should be taken to ensure that process equipment is not isolated from its relief system. To provide continuous pressure relief protection when a device requires maintenance, equipment may be provided with dual relief systems, each sized to provide the total required flow capacity. Stop valves installed between a vessel and its relief device should have a full port area that is at least equal to that of the pressure relief device inlet. These valves should be locked open or have handles removed when the protected vessel is in use. If the discharge is to be piped to a closed disposal system, the pressure drop caused by the additional piping must be considered and the relief device sized accordingly.

Some aspects of the proper placement and use of pressure relief valves have been discussed earlier in this section in conjunction with storage vessels. Additional guidelines for the correct use of pressure relief valves include the following (7):

- Arrangement should be such as to minimize the possibility of tampering with the pressure setting adjustment;

- They should have direct communication with the vapor space of the container;

- When relief valves are put in series, the downstream valves must be large enough to accept the total potential relief capacity;

- Discharge lines of liquid relief valves should not be run to a high point;

- The set-point of a relief valve in the discharge of a pump should be checked to ensure that it is higher than the maximum shut-off pressure of the pump;

- The flow capacity should not be restricted by any connection to it on either the upstream or downstream side; and

- Discharge from pressure relief valves should not terminate in or beneath any building.

Rupture disks may be used to protect pressure relief valves from constant contact with the contents of the storage vessel. Rupture disks should not be used in ammonia service where the ruptured disk discharges directly into the atmosphere. If the disk relieves the contents of the container through a spring-loaded pressure relief valve, a small vent should be provided in the chamber between the disk and the valve to prevent any back pressure on the rupture disk. Because operating pressures exceeding 70% of a disk bursting pressure may induce premature failure, a considerable margin should be allowed when sizing rupture disks.

Instrumentation-- For normal applications, all steel pressure gauges graduated from 0-400 psig are recommended for ammonia service (1). For low pressure work, the range for the gauge should be one and one-half times the maximum service pressure.

The most commonly used flowmeter for ammonia gas is the tapered tube, float type (1). For high pressure work the glass tube should be enclosed in a vented shield or, preferably, a steel-armored type. Orifice meters with differential pressure cells may also be used. Mercury manometers should not be used in ammonia service. The quantity of liquid ammonia transferred from one system to another may be measured with positive displacement or turbine meters.

Magnetic or rotary gauges are preferred to gauge glasses (3). Ammonia should never be closed into a gauge glass, as an increase in pressure may break the glass. Glasses should be equipped with excess flow valves to stop the flow of ammonia if breakage occurs, and they should have automatic self-closing shutoff valves which must be held open to take a reading (3).

Instrument component failures cause about 0.6 plant shutdowns each year (38). It is projected that this can be reduced by 36% by making all single pressure, temperature, flow, and level switches redundant.

5.3.2 Plant Siting and Layout

The siting and layout of a particular ammonia facility is a complex issue which requires careful consideration of numerous factors. These include the other processes in the area, the proximity of population centers, prevailing winds, local terrain, and potential natural external effects such as flooding.

Siting of facilities or individual equipment items should be done in a manner that reduces personnel exposure, both plant and public, in the event of a release. Since there are also other siting considerations, there may be trade-offs between this requirement and others in a process, some directly safety related. Siting should provide ready ingress or egress in the event of an emergency and yet also take advantage of barriers, either man-made or natural which could reduce the hazards of releases. Large distances between large inventories and sensitive receptors is desirable.

Various techniques are available for formally assessing a plant layout and should be considered when planning high hazard facilities (39).

The siting and layout of any facility handling ammonia should adhere to the following general guidelines:

- Areas in which ammonia hazards exist should have an adequate number of well marked exits through which personnel can escape quickly if necessary; doors should open outward and lead to unobstructed passageways;

- The plant is laid out so that, whenever possible, there are no confined spaces between equipment; large distances between large inventories and sensitive receptors is desirable;

- Access to platforms above ground level should be by stairway in preference to cat ladders, and work areas above ground level should have alternative means of escape;

- The ground under process equipment and storage vessels should be sloped so that fire water and liquid spillages flow away from equipment and then into drains, avoiding pools underneath equipment;

- Storage facilities should be located in cool, dry, well-ventilated areas, away from heavily trafficked areas and emergency exits; and

- Tank car, tank truck and storage facilities should be located away from sources of heat, fire and explosion.

Because heat causes thermal expansion of liquid ammonia, measures should be taken to situate piping, storage vessels, and other ammonia equipment so that they are not located adjacent to piping containing flammable materials, hot process piping, equipment, steam lines, and other sources of direct or radiant heat. Special consideration should be given to the location of furnaces and other permanent sources of ignition in the plant. Storage should also be situated away from control rooms, offices, utilities, and laboratory areas.

In the event of an emergency, there should be more than one entry to the facility which is accessible to emergency vehicles and crews. Storage vessel shut-off valves should be readily accessible. Containment for liquid storage tanks can be provided by diking. Dikes reduce evaporation rates while containing the liquid. It is also possible to equip a diked area to allow drainage to an underground containment sump. This sump would be vented to either a recovery or scrubber system for safe removal. A full containment system using a specially constructed building is another possible option. This type of secondary containment could be considered for large volume, liquid ammonia storage tanks.

5.3.3 Transfer and Transport Facilities

Transfer and transport facilities where both road vehicles and rail tankers are loaded or unloaded are likely accident areas because of vehicle movement and the intermittent nature of the operations. Therefore, special attention should be given to the design of these facilities.

Before unloading, tank vehicles should be securely moored; an interlocked barrier system is commonly used. Tank cars must also be protected on both ends by derailers or on the switch end if located on a dead end siding. Sufficient space should be available to avoid congestion of vehicles or personnel during loading and unloading operations. Vehicles, especially trucks, should be able to move into and out of the area without reversing. High curbs around transfer areas and barriers around equipment should be provided to protect equipment from vehicle collisions.

Correct procedures must be followed when unloading and handling small ammonia storage vessels. Dragging, sliding, or rolling cylinders, even for short distances, is not acceptable. Lifting magnets, slings of rope or chain, or any other device in which the cylinders themselves form a part of the carrier should never be used for transporting cylinders.

5.4 PROTECTION TECHNOLOGIES

This subsection describes two types of protection technologies for containment and neutralization. These are:

- Enclosures; and

- Scrubbers.

A presentation of more detailed information on these systems is planned in other volumes of the prevention reference manual series.

5.4.1 Enclosures

Enclosures refer to containment structures which capture any ammonia spilled or vented from storage or process equipment, thereby preventing immediate discharge of the chemical to the environment. The enclosures contain the spilled liquid or gas until it can be transferred to other containment and discharged at a controlled rate which would not be injurious to people or the environment, or transferred at a controlled rate to water scrubbers for absorption.

Specially designed enclosures for ammonia storage or process equipment do not appear to be in widespread use. The principle that it may be preferable to locate toxic operations in the open air has been mentioned in the literature (39), along with the opposing idea that sometimes enclosure may be appropriate. The desirability of enclosure depends partly on the frequency with which personnel must be involved with the equipment. A common design rationale for not having an enclosure where toxic materials are used is to prevent the accumulation of toxic concentrations within enclosed areas. However, if the issue is providing for secondary containment, total enclosure may be appropriate.

If total enclosure is deemed appropriate for a given installation, it should be equipped with continuous monitoring equipment and adequate fire protection. Alarms should sound whenever lethal or flammable concentrations are detected. Care must be taken when an enclosure is built around pressurized equipment. From an economic standpoint, it would not be practical to design an enclosure to withstand the pressures associated with the sudden failure of a pressurized vessel. Therefore, if an enclosure is built around pressurized equipment, it should be equipped with some type of explosion protection, such as rupture plates. These components are designed to fail at a pressure lower than the design pressure of the enclosure, thus preventing the entire structure from failing.

An enclosure would have a ventilation system designed to draw in air when the enclosure was vented. The bottom section of an enclosure which is used for stationary storage containers should be liquid tight to retain any liquid ammonia that might be spilled. Enclosures around rail tank cars which are used for storage do not normally lend themselves easily to effective liquid containment. However, containment can be accomplished if the floor of the enclosure is excavated several feet below the track level while the tracks are supported at grade in the center.

While the use of enclosures for secondary containment of ammonia spills or releases is not known to be widely used, it might be considered for areas near sensitive receptors.

5.4.2 Scrubbers

Scrubbers are a traditional method for absorbing toxic gases from process streams. These devices can be used for the control of ammonia releases from vents and pressure relief discharges, from process equipment, or from secondary containment enclosures.

Because of its high solubility, ammonia discharges could be absorbed in water in any of several types of scrubbing devices. Types of scrubbers that might be appropriate include spray towers, packed bed scrubbers, and venturis. Other types of special designs might be suitable but complex internals subject to corrosion do not seem to be advisable.

Whatever type of scrubber is selected, a complete system would include the scrubber itself, a liquid feed system, and reagent makeup equipment. If such a system is used as protection against emergency releases, consideration must be given to how it would be activated in time to respond to an emergency load. One approach used in some process facilities is to maintain a continuous circulation of scrubbing liquor through the system. For many facilities this would not be practical, and the scrubber system might be tied into a trip system to turn it on when it is needed. However, with this system a quantity of ammonia would be released prior to actuation of the scrubber (i.e., starting up a blower and turning on the flow of liquid).

The scrubber system must be designed so as not to present excessive resistance to the flow of an emergency discharge. The pressure drop should be only a small fraction of the total pressure drop through the emergency discharge system. In general, at the liquid-to-gas ratios required for effective scrubbing, spray towers have the lowest, and venturis the highest pressure drops. While packed beds may have intermediate pressure drops at proper liquid-to-gas ratios, excessive ratios or plugging can increase the pressure drop substantially. However, packed beds have higher removal efficiencies than spray towers or venturis.

In addition, the scrubber system must be designed to handle the "shock wave" generated during the initial stages of the release. This is particularly important for packed bed scrubbers since there is a maximum pressure with which the gas can enter the packed section without damaging the scrubber internals.

Design of emergency scrubbers can follow standard techniques discussed in the literature, carefully taking into account the additional considerations just discussed. An example of the the sizing of an emergency packed bed scrubber is presented in Table 5-3. This example provides some idea of the size of a typical emergency scrubber for various flow rates. This is an

TABLE 5-3. EXAMPLE OF PERFORMANCE CHARACTERISTICS FOR AN EMERGENCY PACKED BED SCRUBBER FOR AMMONIA

Basis: Inlet stream of 50% NH_3 in 50% air. Constant gas flow per unit cross-sectional area of 455 scfm/ft^2.

Packing: 2-inch plastic Intalox® saddles.

Pressure Drop: 0.5 inch water column

Removal Efficiency, %	50	90
Liquid to Gas Ratio (gal/thousand scf)		
— at flooding	160	160
-- operating	80	80
Packed Height, ft.	3.1	11.4

Column Diameter and Corresponding Gas Flow Rates for Both Removal Efficiencies

Column Diameter (ft)	Flow Rate (scfm)
0.5	90
1.0	360
2.0	1,400
6.3	14,000

example only and should not be used as the basis for an actual system which might differ based on site specific requirements.

Another approach is the drowning tower where the ammonia vent is routed to the bottom of a large tank of uncirculating water. The drowning tower does not have the high contact efficiency of the other scrubber types. However, it can provide substantial capacity on demand as long as the back pressure of the hydrostatic head does not create a secondary hazard, by impeding an overpressure relief discharge, for example.

5.5 MITIGATION TECHNOLOGIES

If, in spite of all precautions, a large release of anhydrous ammonia were to occur, the first priority would be to rescue workers in the immediate vicinity of the accident and evacuate persons from downwind areas. The source of the release should be determined, and the leak should be plugged to stop the flow if this is possible. The next primary concern becomes reducing the consequences of the released chemical to the plant and the surrounding community. Reducing the consequences of an accidental release of a hazardous chemical is referred to as mitigation. Mitigation techniques include such measures as physical barriers, water sprays and fogs, and foams. The purpose of a mitigation technique is to divert, limit, or disperse the chemical that has been released to the atmosphere. The mitigation technology chosen for a particular chemical will depend on the specific properties of the chemical including its flammability, toxicity, reactivity, and those properties which determine its dispersion characteristics in the atmosphere.

If a release occurs from a pressurized ammonia storage tank, a quantity of liquid will immediately flash to its atmospheric boiling point producing a vapor/aerosol cloud of ammonia. The remaining liquid will cool to the normal boiling point of -28 °F. Heat transfer from the air and ground will result in further vaporization of the released liquid. Since the ammonia accidentally released from a refrigerated storage tank is already at or below its normal boiling point, a comparable quantity of vapor will not flash off, as with a pressurized release, but heat transfer from the environment will still quickly cause the formation of a vapor cloud. It is therefore desirable to minimize the area available for heat transfer to a liquid spill which in turn will minimize the rate of evaporation. Mitigation technologies which are used to reduce the rate of evaporation of a released liquified gas include secondary containment systems such as impounding basins, dikes, and enclosures.

A post-release mitigation effort requires that the source of the release be accessible to trained plant personnel. Therefore, the availability of adequate personnel protection is essential. Personnel protection will typically include such items as portable breathing air and chemically resistant protective clothing.

5.5.1 Secondary Containment Systems (7,40,41)

Specific types of secondary containment systems include excavated basins, natural basins, earth, steel, or concrete dikes, and high impounding walls. The type of containment system best suited for a particular facility will depend on the risk associated with an accidental release from that location. The inventory of ammonia and its proximity to other portions of the plant and to the community are primary considerations in the selection. The secondary containment system should have the ability to contain spills with a minimum of damage to the facility and its surroundings and with minimum potential for escalation of the event.

While it is common practice to provide ammonia storage tank installations with an earth or concrete dike to contain the liquid into a manageable pool should a total failure of the main tank occur, the efficacy of a dike in the event of a release from pressurized storage has been questioned. This is because a sudden loss of pressurized containment tends to result in ejection of all the contents in the form of vapor, or spray, leaving no residual liquid

(17). There may, however, be situations where a dike would be appropriate for a pressurized ammonia storage vessel.

A conventional dike is of use when refrigerated storage is involved. The liquid is already at atmospheric pressure, and it is assumed that most of the contents of the tank will be contained within the confines of the dike in the event of a release from the tank. ANSI K61.1 requires that one of the following should be provided with any primary refrigerated storage system; it has no similar provisions for pressurized storage (7):

- An adequate drainage system underlying the storage vessels which terminates in an impounding basin having a capacity as large as the largest tank served; or
- A diked area with the capacity as large as the largest tank served.

These measures are designed to prevent accidental discharge of liquid ammonia from spreading to uncontrolled areas.

The most common type of containment system is a low wall earth dike surrounding one or more storage tanks. Generally, no more than three tanks are enclosed within one diked area because of increased risk. Piping should be routed over dike walls, and penetrations through the walls should be avoided if possible. Vapor fences may be situated on top of the dikes to provide additional vapor storage capacity. If there is more than one tank in the diked area, the tanks should be situated on berms above the maximum liquid level attainable in the impoundment.

Dike heights usually range from 3 to 12 feet depending on the area available to achieve the required volumetric capacity. The dike walls should be liquid tight and able to withstand the hydrostatic pressure and temperature of a spill. It may be necessary to construct low wall dikes of low temperature steel or concrete because of adverse soil conditions or other specific requirements. In addition, some experiments have led to the conclusion that earth dikes should be covered with a layer of clay, asphalt, plastic film, or a similar material that is impermeable to liquid ammonia (42). Otherwise, the ammonia will percolate into the ground, and the loss of ammonia by evaporation will be greater in the absence of an impermeable layer over the dike.

A low wall dike can effectively contain the liquid portion of an accidental release and keep the liquid from entering uncontrolled areas. However, a dike also limits access to the tank during a spill. Therefore, a remote impounding basin may be considered if a relatively large site is available within a reasonable distance of the storage system. With such a system, the flow is directed to the basin by dikes and channels under the storage tanks which are designed to minimize exposure of the liquid to other tanks and surrounding facilities. The advantages of this type of system are

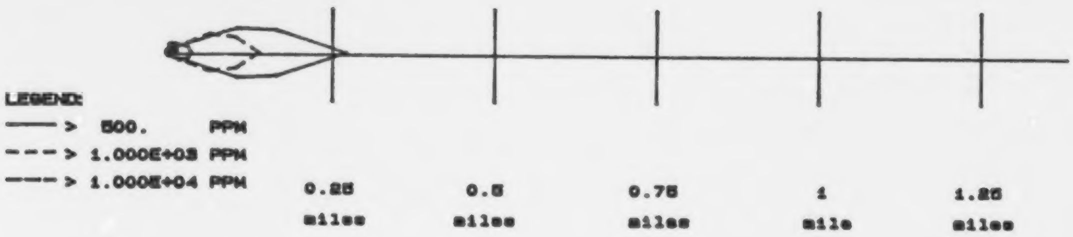
- The spilled liquid is removed from the immediate tank area;
- The probability of the spilled liquid causing further damage to the tank, piping, electrical facilities, pumps, and other equipment is reduced;
- The tank area is accessible during the spill; and
- Access to the tank pumps or related piping for regular operation, inspection, or maintenance is not restricted by the impoundment.

The impounding basin may be located to use the natural topography of the area thus minimizing additional excavation and diking. A sump can also be provided within the main impounding basin to limit the liquid surface and ground contact areas. Furthermore, the depth of the basin can be increased to provide vapor containment.

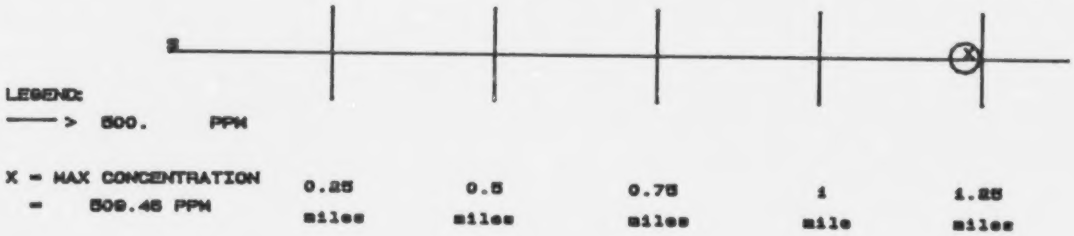
Although few authorities for ammonia facilities require them, high wall impoundments may be the best secondary containment choice for selected systems. Circumstances which may warrant their use include limited storage site area, the need to minimize vapor generation rates, and/or the tank must be protected from external hazards. Maximum vapor generation rates will generally be lower for a high wall impoundment than for low wall dikes or remote impoundments because of the reduced surface contact area. These rates can be further reduced with the use of insulation on the wall and floor in the annular space. High impounding walls may be constructed of low temperature steel, reinforced concrete, or prestressed concrete. A weather shield may be provided between the tank and wall with the annular space remaining open to the atmosphere. The available area surrounding the storage tank will dictate the minimum height of the wall. The walls may be designed with a volumetric capacity greater than that of the tank to provide vapor containment. Increasing the height of the wall also raises the elevation of any released vapor.

One disadvantage of these dikes is that high walls around a tank may hinder routine external observation. Furthermore, the closer the wall is to the tank, the more difficult it becomes to access the tank for inspection and maintenance. As with low wall dikes, piping should be routed over the wall if possible. The closeness of the wall to the tank may necessitate placement of the pump outside of the wall, in which case the tank outlet (suction) line will have to pass through the wall. In such a situation, a low dike encompassing the pipe penetration and pump may be provided, or a low dike may be placed around the entire wall.

An example of the effect of diking as predicted by a vapor dispersion model is shown in Figure 5-1 (43). This figure shows ammonia vapor clouds at the time when the farthest distance away from the source is exposed to concentrations above the IDLH. With diking, the model predicts that downwind



Release from a tank surrounded by a 25 ft. diameter dike.
Elapsed Time: 2 minutes



Release from a tank with no dike.
Elapsed Time: 8 minutes

Common Release Conditions

Storage Temperature = 85°F
Storage Pressure = 148 psig
Ambient Temperature = 85°F

Wind Speed = 10 mph
Atmospheric Stability Class = C
Quantity Released = 5000 gallons through a 2-inch hole

Figure 5-1. Computer model simulation showing the effect of diking on the vapor cloud generated from a release of liquified ammonia.

distances up to 1400 feet from the source of the release could be exposed to concentrations above the IDLH. Two minutes are required for the vapors to reach the maximum down wind distance. Without diking, the model predicts that downwind distances up to 6600 feet from the source could be exposed to concentrations above the IDLH. Eight minutes are required for the vapors to reach this distance.

One further type of secondary containment system is one which is structurally integrated with the primary system and forms a vapor tight enclosure around the primary container. Many types of arrangements are possible. These systems may be considered where protection of the primary container and containment of vapor for events not involving foundation or wall penetration failure are of greatest concern. Drawbacks of an integrated system are the greater complexity of the structure, the difficulty of access to certain components, and the fact that complete vapor containment cannot be guaranteed for all potential events.

Provision should be made for drainage of rainwater from both impounding basins and diked areas. This will involve the use of sumps and separate drainage pumps, since direct drainage to stormwater sewers would presumably allow any spilled ammonia to follow the same route. Alternately, a sloped rain hood may be used over the diked area which could also serve to direct the rising vapors to a single release point (41). The ground within the enclosure should be graded to cause the spilled liquid to accumulate at one side or in one corner. This will help to minimize the area of ground to which the liquid is exposed and from which it may gain heat. In areas where it is critical to minimize vapor generation, surface insulation may be used in the diked area or impoundment to further reduce heat transfer from the environment to the spilled liquid. The floor of an impoundment should be sealed with a clay blanket to prevent the ammonia from seeping into the ground; percolation into the ground causes the ground to cool more quickly, increasing the vapor generation rate. Absorption of the ammonia into water in the soil would also release additional heat.

5.5.2 Flotation Devices and Foams (42,44,45,46)

Other possible means of reducing the surface area of spilled liquid ammonia include placing impermeable flotation devices on the surface, dilution with water, and applying water-based foams.

Placing a lid over a spilled chemical is a direct approach for containing the toxic vapors with nearly 100 percent efficiency. The floating cover may be continuous or a distribution of light particulates. However, being able to use these techniques requires acquisition in advance of the spill and storage until needed, and in all but small spills deployment may be difficult. Furthermore, although particulate covers are potentially effective, cost is a deterrent to their use. Determination of appropriate materials for application to an ammonia spill has been the subject of some research (42), but the use of mechanical barriers on an actual spill has not been reported in the literature.

One approach to an ammonia spill is dilution with water, but, because of the high heat of solution, the addition of pure water would result in a violent boil-off of ammonia. A water-based foam cover provides a means of diluting the ammonia with a minimum heat of solution, because water is added at a slow rate. While the use of foams in vapor hazard control has been demonstrated for a broad range of volatile chemicals, it is difficult to accurately quantify the benefits of foam systems, because the effects will vary as a function of the chemical spilled, foam type, spill size, and atmospheric conditions. With regard to liquified gases, it has been found that with some materials, foams have a net positive effect, but with others, foams may exaggerate the hazard.

When a foam cover is first applied, an increase in the boil off rate is generally observed which causes a short-term increase in the downwind ammonia concentration. The initial foam cover may be destroyed by violent boiling, in which case a second application is necessary. Once a continuous layer is formed, a net positive effect will be achieved in the downwind area (44). The reduction in downwind concentration is a result of both increased dilution with air, because of a reduced vaporization rate, and the increased buoyancy of the vapor cloud. This latter effect is a result of the vapor being warmed as it rises through the blanket by heat transfer from the foam and by the heat of solution of ammonia in water; the warmed vapor cloud will have greater buoyancy and will disperse in an upward direction more rapidly.

The extent of the downwind reduction in concentration will depend on the type of foam used. Research in this area has indicated that medium to high expansion foams (75 to 350:1) give significantly better results than do low expansion foams (6 to 8:1) (44,45). Furthermore, a high expansion foam will cause a smaller initial increase in boil off than a low expansion foam.

Regardless of the type of foam used, the slower the drainage rate of the foam, the better its performance will be. A slow draining foam will spread more evenly, show more resistance to temperature and pH effects, and collapse more slowly. The initial cost for a slowly draining foam may be higher than for other foams, but a cost effective system will be realized in superior performance.

5.5.3 Mitigation Techniques for Ammonia Vapor (47,48)

The extent to which the escaped ammonia vapor can be removed or dispersed in a timely manner will be a function of the quantity of vapor released, the ambient conditions, and the physical characteristics of the vapor cloud. The behavior and characteristics of the ammonia cloud will be dependent on a number of factors. These include the physical state of the ammonia before its release, the location of the release, and the atmospheric and environmental conditions. Many possibilities exist concerning the shape and motion of the vapor cloud, and a number of predictive models of dispersion have been developed. In spite of the lower specific gravity of pure ammonia vapor, large accidental releases of ammonia have often resulted in the formation of ammonia-air mixtures which are denser than the surrounding atmosphere. This type of vapor cloud is especially hazardous, because it will spread laterally and remain close to the ground.

The primary means of dispersing as well as removing ammonia vapor from the air is with the use of water sprays or fogs. The water is applied to the vapor cloud by means of hand-held hoses and/or stationary water-spray barriers. For effective absorption, it is important to direct waterfog or spray nozzles from a downwind direction to avoid driving the vapors downwind more quickly. Other important factors relating to the effectiveness of water sprays are the distance of the nozzles from the point of release, the fog pattern, nozzle flow rate, pressure, and nozzle rotation. If the right strategy is followed, a "capture zone" can be created downwind of the release into which the ammonia vapor will drift and be absorbed. In low wind conditions, two fog nozzles should be placed upwind of the release to ensure that the ammonia cloud keeps moving downwind against the water fog nozzle pressures. If water fog is used to absorb ammonia vapors from a diked area containing spilled liquid ammonia, great care must be taken not to direct water into the liquid ammonia itself.

Water-spray barriers consist of a series of spray nozzles which can be directed either up or down. If placed 30-40 feet from the point of ammonia release, these barriers are very effective in absorbing the ammonia vapors passing through without distortion of the ammonia cloud (47). Several fog nozzles may be situated farther downwind to absorb the remainder of the vapors getting through.

In general, techniques used to disperse or control vapor emissions should emphasize simplicity and reliability. In addition to the mitigation techniques discussed above, physical barriers such as buildings and rows of trees will help to contain the vapor cloud and control its movement. Hence, reducing the consequences of a hazardous vapor cloud can actually begin with a carefully planned layout of facilities and the use of imaginative landscaping around major hazard sites.

5.6 OPERATION AND MAINTENANCE PRACTICES

Accidental releases of toxic materials result not only from deficiencies of design but also from deficiencies of operation. Unfortunately, human error is often responsible for the realization of hazards with potentially damaging consequences. The human error hazard manifests itself in numerous ways, both indirectly and directly. For example, a lax management policy which does not enforce safety standards might be indirectly responsible for an unnecessary injury or fatality, or an operator may take the wrong action at a control panel which would directly lead to a hazardous release. Aspects of plant operation which impact the magnitude of the risk of human error include management policy, operator training, and maintenance and modification procedures. These topics are discussed in the following subsections.

5.6.1 Management Policy

Competent and effective management plays a vital role in the prevention of accidental releases as a result of human error. The primary responsibilities of managers at chemical plants with large inventories of hazardous chemicals include the following (39):

- Ensuring worker competency;
- Developing, documenting, and enforcing standard operating procedures and safety policies;
- Communicating and promoting feedback regarding safety issues;
- Identification, assessment, and control of hazards; and

- Regular plant audits and provisions for independent checks.

Management is ultimately responsible for the competency of workers hired at facilities which handle hazardous materials. Because of the serious consequences that may result from operator error at these installations, the qualifications and capabilities of prospective personnel for high hazard areas should be carefully assessed to ensure that worker skills are matched to job responsibilities. In addition, the skills of competent operators should be maintained by regular training, safety meetings, and employee reviews.

In the chemical industry, documentation is generally produced which sets forth standard procedures for equipment operation, maintenance, inspection, hazard identification, and emergencies. The enforcement of standard procedures is therefore one of management's most fundamental responsibilities in the area of plant safety and accident prevention. However, before procedures can be enforced, they must be communicated to plant personnel in a clear, concise style so that they are thoroughly understood. Emphasis should be placed on worker safety and the serious consequences of operator error in processes involving hazardous materials.

Unfortunately, requiring workers to read documents which contain safety policies is often not enough to ensure that they are fully understood and followed. For this reason, verbal communication should be practiced and encouraged which emphasizes plant safety and promotes feedback. When management demonstrates a willingness to respond to initiatives from below and participates directly with workers in improving safety, worker morale increases, influencing the degree to which standard procedures are followed.

Hazard identification, assessment, and control is another area that should be addressed by management to minimize the potential for accidental chemical releases. The establishment of formal hazard assessment techniques would provide management with a mechanism for obtaining information which can be used to rank potential problems and decide how best to allocate hazard control resources.

The plant safety audit is one of the most frequently used methods for obtaining safety related information. A total plant safety audit involves a thorough evaluation of a plant's design, layout, and procedures, and is specifically aimed at identifying and correcting potentially unsafe conditions. The objectives of these audits include alerting operating personnel to process hazards, determining if safety procedures need to be modified, screening for equipment or process changes that may have introduced new hazards, assessing the feasibility of applying new hazard control technologies, identifying additional hazards, and reviewing inspection and maintenance programs (49). In-house safety audits can be performed by appointed safety review committees, or qualified consultants or insurers may be brought in to provide a more objective assessment.

5.6.2 Operator Training

Accidental chemical releases may result from numerous types of operator errors including following incorrect operating procedures, failing to recognize critical situations, or by direct physical mistakes, e.g., by turning the wrong valve. For all of these errors, the fundamental problem may be the operator's lack of knowledge or understanding of process variables, equipment operation, or emergency procedures. It is important for management to recognize the extent to which a comprehensive operator training program can decrease the potential for accidental releases resulting from human error. Some general characteristics of quality industrial training programs include the following:

- Establishment of good working relations between management and personnel;
- Definition of trainer responsibilities and training program goals;

- Use of documentation, classroom instruction, and field training (in some cases supplemented with simulator training);

- Inclusion of procedures for normal startup and shutdown, routine operations, and emergencies; and

- Frequent supplemental training and the use of up-to-date training materials.

Employees in plants which manufacture, process, or store anhydrous ammonia should be thoroughly educated about the important aspects of handling this chemical. These include the proper means of handling and storing, potential consequences of improper use and handling, prevention of spills, cleanup procedures, maintenance procedures, and emergency procedures. It is the job of the trainer to ensure that the right type and amount of information is supplied at the right time. To do this he must not only understand the technical content of a job, but also those aspects of the job where operators may have difficulty. It is therefore advantageous for trainers to spend time observing and analyzing the tasks and skills they will be teaching.

Two types of training which are especially important cover emergencies and safety procedures. Emergency training includes topics such as:

- Recognition of alarm signals;

- Performance of specific functions (e.g., shutdown switches);

- Use of emergency equipment;

- Evacuation procedures;

- Fire fighting; and

- Rehearsal of emergency situations.

Safety training includes not only responses to emergency situations, but also accident prevention measures. Aspects addressed in safety training sessions include (39):

- Hazard recognition and communication;
- Actions to be taken in particular situations;
- Available safety equipment and locations;
- When and how to use safety equipment;
- Use and familiarity with relevant documentation; and
- First aid and CPR.

The frequency of training and the frequency with which training materials are updated are important in maintaining strong training programs. Chemical processes may be modified to the extent that equipment changes require operational change, and operators must be made aware of the changes and safety considerations that accompany them in a timely manner. In addition to operator training programs, organized management training is also beneficial as it provides managers with the perspective necessary to formulate good policies and procedures and to make changes that will improve the quality of the overall plant safety program.

5.6.3 Maintenance and Modification Practices

Plant maintenance is necessary to ensure the structural integrity of chemical processing equipment; modifications are often necessary to allow more effective production. However, since these activities are also potential causes of accidental chemical releases, proper maintenance and modification practices are important to the prevention of accidents.

Maintenance refers to a wide range of activities, including preventive maintenance, production assistance (e.g., adjustment of settings), servicing (e.g., lubrication and replacement of consumables), running maintenance, scheduled repairs during shutdown, and breakdown maintenance. These activities in turn require specific operations such as emptying, purging, and cleaning vessels, breaking pipelines, tank repair or demolition, welding, hot tapping (attaching a branch to an in-service line), and equipment removal (39).

Proper maintenance and modification programs should be a normal part of plant operation and design procedures, respectively, to reduce the chances for an accidental release. Maintenance should be based on a priority system to ensure that the most critical equipment is taken care of first. Strict procedures should apply to process modifications to ensure that modifications do not create unintended hazards. Inspections and nondestructive testing of vessels, piping, and machinery should be conducted periodically to detect small flaws that could eventually lead to a major release.

Two of the more common maintenance problems are equipment identification and equipment isolation (39). Work performed on the wrong piece of equipment can have disastrous effects, as can failure to completely isolate equipment from process materials and electrical connections. Other potential sources of maintenance accidents are improper venting to relieve pressure, insufficient draining, and not cleaning or purging systems before maintenance activities begin.

Permit systems and up-to-date maintenance procedures minimize the potential for accidents during maintenance operations. Permit-to-work systems control maintenance activities by specifying the work to be done, defining individual responsibilities, eliminating or protecting against hazards, and ensuring that appropriate inspection and testing procedures are followed. Such permits generally include specific information such as (39):

- The type of maintenance operations to be conducted,
- Descriptions and identifying codes of the equipment to be worked on,
- Classification of the area in which work will be conducted,
- Documentation of special hazards and control measures,
- Listing of the maintenance equipment to be used, and
- The date and time when maintenance work will be performed.

Permit-to-work systems offer many advantages. They explain the work to be done to both operating and maintenance workers. In terms of equipment identification and hazard identification, they provide a level of detail that significantly reduces the potential for errors that could lead to accidents or releases. They also serve as historical records of maintenance activities.

Another form of maintenance control is the maintenance information system. Ideally, these systems should log the entire maintenance history of equipment, including preventative maintenance, inspection and testing, routine servicing, and breakdown or failure maintenance. This type of system is also used to track incidents caused by factors such as human error, leaks, and fires which resulted in hazardous conditions, downtime, or direct repair costs.

One important maintenance practice is repairing or replacing equipment that appears to be headed for failure. A number of testing methods are available for examining the condition of equipment. Some of the most common types of tests are listed below:

- Metal thickness and integrity testing,
- Vibration testing and monitoring, and
- Relief valve testing.

All of the above testing procedures are nondestructive, i.e., they do not damage the material or equipment that they test.

Accidental releases are frequently the result of some aspect of plant modification. To avoid confusion with maintenance activities, a modification is defined as an intentional change in process materials, equipment, operating procedures, or operating conditions (39). Accidents result when equipment integrity and operation are not properly assessed following modification, or when modifications are made without updating corresponding operation and maintenance instructions. Frequently, hazards created by modifications do not appear in the exact location of the change. For example, equipment modifications can invalidate the arrangements for system pressure relief and blowdown or they can invalidate the function of instrumentation systems. Several factors should be considered in reviewing modification plans before authorizing work. According to Lees, these include (39):

- Sufficient number and size of relief valves,
- Appropriate electrical area classification,
- Elimination of effects which could reduce safety standards,
- Use of appropriate engineering standards,

- Proper materials of construction and fabrication standards,
- Existing equipment not stressed beyond design limits,
- Necessary changes in operating conditions, and
- Adequate instruction and training of operation and maintenance teams.

5.7 CONTROL EFFECTIVENESS

It is difficult to quantify the control effectiveness of preventive and protective measures to reduce the probability and magnitude of accidental releases. Preventive measures, which may involve numerous combinations of process design, equipment design, and operational measures, are especially difficult to quantify because they reduce a probability rather than a physical quantity of a chemical release. Protective measures are more analogous to traditional pollution control technologies. Thus, they may be easier to quantify in terms of their efficiency in minimizing the adverse effects of a chemical that could be released.

Preventive measures reduce the probability of an accidental release by increasing the reliability of both process systems operations and the equipment. Control effectiveness can thus be expressed for both the qualitative improvements and the quantitative improvements through probabilities. Table 5-4 summarizes what appear to be some of the major design, equipment, and operational measures applicable to the primary hazards identified for the ammonia applications in the U.S. The items listed in this table are for illustration purposes only and do not necessarily represent a satisfactory control option for all cases. These control options appear to reduce the risk associated with an accidental release when viewed from a broad perspective. However, there are undoubtedly specific cases where these control options will not be appropriate. Each case must therefore be evaluated individually. A presentation of more information about reliability in terms of probabilities is planned for other volumes of the prevention reference manual series.

5.8 ILLUSTRATIVE COST ESTIMATES FOR CONTROLS

This section presents cost estimates for different levels of control and for specific release prevention and protection measures for ammonia storage and process facilities found in the United States.

5.8.1 Prevention and Protection Measures

Preventive measures reduce the probability of an accidental release from a process or storage facility by increasing the reliability of both process systems operations and equipment. Along with an increase in the reliability of a system is an increase in the capital and annual costs associated with incorporating prevention and protection measures into a system. Table 5-5 presents costs for some of the major design, equipment, and operational measures applicable to the primary hazards identified in Table 5-4 for the ammonia applications discussed in Section 3.

5.8.2 Levels of Control

Prevention of accidental releases relies on a combination of technological, administrative, and operational practices as they apply to the design, construction, and operation of facilities where hazardous chemicals are used and stored. Inherent in determining the degree to which these practices are carried out is their costs. At a minimum, equipment and procedures should be in accordance with applicable codes, standards, and regulations. However, additional measures can be taken to provide extra protection against an accidental release.

The levels of control concept provides a means of assigning costs to increased levels of prevention and protection. The minimum level is referred

TABLE 5-4. EXAMPLES OF MAJOR PREVENTION AND PROTECTION MEASURES FOR AMMONIA RELEASES

Hazard Area	Prevention/Protection
Ammonia flow control	Redundant flow control loops; Minimal overdesign of feed systems
Temperature sensing and cooling medium flow control	Redundant temperature sensors; Interlock flow switch to shut off NH_3 feed on loss of cooling, with relief venting to emergency scrubber system
Temperature sensing and heating medium flow control	Redundant temperature sensors; Interlock flow switch to shut off NH_3 feed on loss of heating, with relief venting to emergency scrubber system
Overpressure	Redundant pressure relief; not isolatable; adequate size; discharge not restricted
Corrosion	Increased monitoring with more frequent inspections; use of corrosion coupons; visual inspections; non-destructive testing
Reactor and reboiler temperatures	Redundant temperature sensing and alarms
Overfilling	Redundant level sensing, alarms and interlocks; training of operators
Atmospheric releases from relief discharges	Emergency vent scrubber system
Storage tank or line rupture	Diking; foams; dilution; neutralization; water sprays; enclosure vented to emergency scrubber system

TABLE 5-5. ESTIMATED TYPICAL COSTS OF MAJOR PREVENTION AND PROTECTION MEASURES FOR AMMONIA RELEASE[a]

Prevention/Protection Measure	Capital Cost (1986 $)	Annual Cost (1986 $/yr)
Flow control loop	4,000-6,000	500-750
Temperature sensor	250-400	30-50
Pressure relief		
- relief valve	1,000-2,000	120-250
- rupture disk	1,000-1,200	120-150
Interlock system for flow shut-off	1,500-2,000	175-250
Alarm system	250-500	30-75
Level sensor		
- liquid level gauge	1,500-2,000	175-250
- load cell	10,000-15,000	1,300-1,900
Physical barriers		
- curbing	750-1,000	120-150
- 3 ft. retaining wall	1,500-2,000	175-250
Diking (based on a 10,000 gal. tank)		
- 3 ft. high	1,200-1,500	150-175
- top of tank height, 10 ft.	7,000-7,500	850-900
Increased corrosion inspection[b]		200-400

[a] Based on a 10,000 gallon fixed ammonia storage tank system and a 10 tons/day ammonia stripper system.

[b] Based on 10-20 hours @ $20/hr.

to as the "Baseline" system. This system consists of the elements required for normal safe operation and basic prevention of an accidental release of hazardous material.

The second level of control is "Level 1". "Level 1" includes the baseline system with added modifications such as improved materials of construction, additional controls, and generally more extensive release prevention measures. The costs associated with this level are higher than the baseline system costs.

The third level of control is "Level 2". This system incorporates both the "Baseline" and "Level 1" systems with additional modifications designed specifically for the prevention of an accidental release such as alarm and interlock systems. The extra accidental release prevention measures incorporated into "Level 2" are reflected in its cost, which is much higher than that of the baseline system.

When comparing the costs of the various levels of control, it is important to realize that higher costs do not necessarily imply improved safety. The measures applied must be applied correctly. Inappropriate modifications or add-ons may not make a system safer. Each added control option increases the complexity of a system. In some cases, the hazards associated with the increased complexity may outweigh the benefits derived from the particular control option. Proper design and construction along with proper operational practices are needed to assure safe operation.

Levels of control cost estimates were prepared for a 25 ton fixed ammonia storage tank system with a 10,000 gal capacity and a waste water treatment ammonia stripper system with a 10 tons/day ammonia recovery rate. The reader should be aware that the cost estimates presented in this section are for illustrative purposes only, i.e., it is doubtful that any specific installation would find all of the control options listed in these tables appropriate for their purposes. An actual system is likely to incorporate some items from each of the levels of control and also some control options not listed here. The purpose of these estimates is to illustrate the relationship between cost and control, not to provide an equipment check list.

5.8.3 Cost Summaries

Table 5-6 presents a summary of the total capital and annual costs for each of the three levels of controls for the ammonia storage system and the ammonia stripper system. The costs presented correspond to the systems described in Table 5-7 and Table 5-8. Each of the level costs include the cost of the basic system plus any added controls. Specific cost information and breakdown for each level of control for both the storage and process facilities are presented in Tables 5-9 through 5-14.

5.8.4 Equipment Specifications and Detailed Costs

Equipment specifications and details of the capital cost estimates for the ammonia storage and the ammonia stripper systems are presented in Tables 5-15 through 5-22.

5.8.5 Methodology

Format for Presenting Cost Estimates--

Tables are provided for control schemes associated with storage and process facilities for ammonia showing capital, operating, and total annual costs. The tables are broken down into subsections comprising vessels, piping and valves, process machinery, instrumentation, and procedures and practice. The presentation of the costs in this manner allows for easy comparison of costs for specific items, different levels, and different systems.

Capital Cost--All capital costs presented in this report are shown as total fixed capital costs. Table 5-23 defines the cost elements comprising total fixed capital as it is used here.

TABLE 5-6. SUMMARY COST ESTIMATES OF POTENTIAL LEVELS OF CONTROLS FOR AMMONIA STORAGE TANK AND STRIPPER

System	Level of Control	Total Capital Cost (1986 $)	Total Annual Cost (1986 $/yr)
Ammonia Storage Tank; 25 Ton Fixed Ammonia Tank with 10,000 Gallon Capacity	Baseline	215,000	26,000
	Level #1	553,000	65,000
	Level #2	1,254,000	146,000
Waste Water Treatment Ammonia Stripper with 10 Tons/Day Ammonia Recovery	Baseline	430,000	59,000
	Level #1	948,000	120,000
	Level #2	1,760,000	197,000

TABLE 5-7. EXAMPLE OF LEVELS OF CONTROL FOR AMMONIA STORAGE TANK

Process: 25 ton fixed ammonia storage tank
10,000 gal

Controls	Baseline	Level No. 1	Level No. 2
Process:	None	None	None
Flow:	Single check-valve on tank-process feed line.	Add second check valve.	Add a reduced-pressure device[a] with internal air gap and relief vent to containment tank or scrubber.
Temperature:	None	None	Add temperature indicator.
Pressure:	Single pressure relief valve, vent to atmosphere. Provide local pressure indicator.	Add second relief valve, secure non-isolatable. Vent to limited scrubber.	Add rupture disks under relief valves. Provide local pressure indication on space between disk and valve.
Quantity:	Local level indicator.	Add remote level indicator.	Add level alarm. Add high-low level interlock shut-off for both inlet and outlet lines.
Location:	Away from traffic.	Away from traffic and flammables.	Away from traffic, flammables, and other hazardous processes.
Materials of Construction:	Carbon steel	Carbon steel with increased corrosion allowances. (1/8 inch)	Type 316 SS.
Vessel:	Tank pressure specification: 250 psig.	Tank pressure specification: 300 psig.	Tank pressure specification: 375 psig

(Continued)

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[a] A reduced pressure device is a modified double check valve

TABLE 5-7 (Continued)

Process: 25 ton fixed ammonia storage tank
10,000 gal

Controls	Baseline	Level No. 1	Level No. 2
Piping:	Schedule 40 carbon steel.	Schedule 80 carbon steel.	Schedule 80 Type 316 stainless steel.
Process Machinery:	Centrifugal pump, carbon steel, stuffing box seal.	Centrifugal pump, 316 SS construction, double capacity mechanical seal.	Magnetically-coupled centrifugal pump, 316 SS, construction.
Enclosures:	None	Steel building.	Concrete building.
Diking:	None	3 ft high.	Top of tank height, 10 ft.
Scrubbers:	None	Water scrubber.	Same.
Mitigation:	None	Water sprays.	Same.

TABLE 5-8. EXAMPLE OF LEVELS OF CONTROL FOR AMMONIA STRIPPER

Process: Waste water Treatment

Basis: 10 tons/day ammonia recovery plant

Controls	Baseline	Level No. 1	Level No. 2
Process:		Enhanced temperature and flow control.	Computer control of process. Use of interlock systems.
Temperature:	Provide local temperature control.	Add redundant temperature sensors and alarms. Add remote temperature indicator.	Add computer control. Add temperature switch and back-up cooling system.
Pressure:	Provide local pressure control. Single pressure relief valve. Vent to atmosphere.	Add redundant pressure sensors. Add second relief valve. Vent to limited scrubber.	Add computer control. Add rupture disks under relief valves and provide local and remote pressure indicator on space between disk and valve.
Flow:	Provide local flow control on stripper feed and heating medium to reboiler.	Add redundant flow control loops.	Add computer control. Add interlock flow switch to shut off feed on loss of cooling medium.
Quantity:	None.	None.	None.
Mixing:	None.	None.	None.
Corrosion:	Visual inspections.	Same.	Same.
Composition:	None.	None.	None.
Materials of Construction:	Carbon steel.	Carbon steel with added corrosion allowance.	Type 316 stainless steel.

(Continued)

TABLE 5-8 (Continued)

Process: Waste water Treatment

Basis: 10 tons/day ammonia Recovery Plant

Controls	Baseline	Level No. 1	Level No. 2
Vessel:	Pressure specification: 250 psig.	Pressure specification: 300 psig.	Pressure specification: 375 psig.
Piping:	Schedule 40 carbon steel.	Schedule 80 carbon steel.	Schedule 80 Type 316 stainless steel.
Process Machinery:	Centrifugal pump, carbon steel construction, stuffing box.	Centrifugal pump. Type 316 stainless steel construction, double capacity mechanical seal.	Magnetically-coupled centrifugal pump, Type 316 stainless steel construction.
Protective Barriers:	None.	Curbing around stripper.	3 ft. high retain- ing wall.
Scrubbers:	None.	Water scrubber.	Same.
Mitigation:	None.	Water sprays.	Same.

TABLE 5-9. ESTIMATED TYPICAL CAPITAL AND ANNUAL COSTS ASSOCIATED WITH BASELINE AMMONIA STORAGE SYSTEM

	Capital Cost (1986 $)	Annual Cost (1986 $/yr)
Vessels:		
Storage Tank	186,000	22,000
Piping and Valves:		
Pipework	4,500	520
Check Valve	520	60
Ball Valves (5)	3,200	370
Excess Flow Valves (2)	950	110
Angle Valves (2)	3,600	420
Relief Valve	2,000	230
Process Machinery:		
Centrifugal Pump	10,000	1,200
Instrumentation:		
Pressure Gauges (4)	1,500	170
Liquid Level Gauge	1,500	170
Procedures and Practices:		
Visual Tank Inspection (external)		15
Visual Tank Inspection (internal)		60
Relief Valve Inspection		15
Piping Inspection		300
Piping Maintenance		120
Valve Inspection		30
Valve Maintenance		350
Total Costs	215,000	26,000

TABLE 5-10. ESTIMATED TYPICAL CAPITAL AND ANNUAL COSTS ASSOCIATED WITH LEVEL 1 AMMONIA STORAGE SYSTEM

	Capital Cost (1986 $)	Annual Cost (1986 $/yr)
Vessels:		
Storage Tank	220,000	26,000
Piping and Valves:		
Pipework	12,000	1,300
Check Valve	1,100	120
Ball Valves (5)	3,200	370
Excess Flow Valves (2)	950	110
Angle Valves (2)	3,600	420
Relief Valves (2)	4,000	460
Process Machinery:		
Centrifugal Pump	20,000	2,300
Instrumentation:		
Pressure Gauges (4)	1,500	170
Flow Indicator	3,700	430
Load Cell	1,500	170
Remote Level Indicator	1,900	220
Enclosures:		
Steel Building	10,000	1,200
Scrubbers:		
Water Scrubber	268,000	31,000
Diking:		
3 ft	1,300	160

(Continued)

TABLE 5-10 (Continued)

	Capital Cost (1986 $)	Annual Cost (1986 $/yr)
Procedures and Practices:		
Visual Tank Inspection (external)		15
Visual Tank Inspection (internal)		60
Relief Valve Inspection		30
Piping Inspection		300
Piping Maintenance		120
Valve Inspection		35
Valve Maintenance		400
Total Costs	553,000	65,000

TABLE 5-11. ESTIMATED TYPICAL CAPITAL AND ANNUAL COSTS ASSOCIATED WITH LEVEL 2 AMMONIA STORAGE SYSTEM

	Capital Cost (1986 $)	Annual Cost (1986 $/yr)
Vessels:		
Storage Tank	877,000	102,000
Piping and Valves:		
Pipework	6,000	680
Reduced Pressure Device	2,700	310
Ball Valves (5)	3,200	370
Excess Flow Valves (2)	950	110
Angle Valves (2)	3,600	420
Relief Valves (2)	4,000	460
Rupture Disks (2)	1,100	130
Process Machinery:		
Centrifugal Pump	32,000	3,700
Instrumentation:		
Temperature Indicator	2,200	260
Pressure Gauges (6)	2,200	260
Flow Indicator	3,700	430
Load Cell	16,000	1,800
Remote Level Indicator	1,900	220
Level Alarm	740	90
High-Low Level Shutoff	1,900	220
Enclosures:		
Concrete Building	19,000	2,200
Scrubbers:		
Alkaline Scrubber	268,000	31,000
Diking:		
10 ft High Concrete Dike	7,400	870

(Continued)

TABLE 5-11 (Continued)

	Capital Cost (1986 $)	Annual Cost (1986 $/yr)
Procedures and Practices:		
Visual Tank Inspection (external)		15
Visual Tank Inspection (internal)		60
Relief Valve Inspection		50
Piping Inspection		300
Piping Maintenance		120
Valve Inspection		35
Valve Maintenance		400
Total Costs	1,254,000	146,000

TABLE 5-12. ESTIMATED TYPICAL CAPITAL AND ANNUAL COSTS ASSOCIATED WITH BASELINE WASTE WATER TREATMENT AMMONIA STRIPPER

	Capital Cost (1986 $)	Annual Cost (1986 $/yr)
Equipment:		
Vessels and Machinery:		
Stripping Column		
Reboiler and Condenser		
Centrifugal Pumps (3)		
Total Vessels and Machinery[a]	260,000	31,000
Piping and Valves:	117,000	14,000
Instrumentation:[a]	53,000	6,000
Maintenance and Inspections:[a]		8,000
Total Costs	430,000	59,000

[a] Costs are based on using cost factors from Peters and Timmerhaus (50) and a total fixed capital cost of $1.8 million (1986 basis) (21) for a 10 tons/day ammonia recovery plant.

TABLE 5-13. ESTIMATED TYPICAL CAPITAL AND ANNUAL COSTS ASSOCIATED WITH LEVEL 1 WASTE WATER TREATMENT AMMONIA STRIPPER

	Capital Cost (1986 $)	Annual Cost (1986 $/yr)
Equipment:		
Vessels and Machinery:		
Stripping Column		
Reboiler and Condenser		
Centrifugal Pumps (3)		
Total Vessels and Machinery[a]	470,000	56,000
Piping and Valves:[a]	147,000	17,000
Relief Valve	2,000	240
Instrumentation:[a]	53,000	6,000
Temperature Sensor	360	45
Temperature Alarm	360	45
Remote Temp. Indicator	1,800	220
Remote Press. Indicator	1,800	220
Flow Control Loops (2)	11,000	1,300
Diking:		
Curbing Around Reactor	1,200	150
Scrubber:		
Water Scrubber	260,000	31,000
Maintenance and Inspections:[a]		8,000
Relief Valve Inspection		15
Total Costs	948,000	120,000

[a] Costs are based on using cost factors from Peters and Timmerhaus (50) and a total fixed capital cost of $1.8 million (1986 basis) (21) for a 10 tons/day) ammonia recovery plant.

TABLE 5-14. ESTIMATED TYPICAL CAPITAL AND ANNUAL COSTS ASSOCIATED WITH LEVEL 2 WASTE WATER TREATMENT AMMONIA STRIPPER

	Capital Cost (1986 $)	Annual Cost (1986 $/yr)
Equipment:		
Vessels and Machinery:		
Stripping Column		
Reboiler and Condenser		
Centrifugal Pumps (3)		
Total Vessels and Machinery[a]	1,049,000	126,000
Piping and Valves[a]:	167,000	20,000
Relief Valve (2)	7,400	880
Rupture Disk (2)	2,300	280
Instrumentation[a]:	53,000	6,400
Temperature Sensor	360	45
Temperature Alarm	360	45
Temperature Switch	540	65
Remote Temp. Indicator	1,800	220
Remote Press. Indicator	1,800	220
Flow Control Loops (2)	11,000	1,300
Flow Interlock System	1,800	220
All Loops on Computer Control[b]	201,000	2,400
Diking:		
3 ft High Retaining Wall	3,000	360
Scrubber:		
Water Scrubber	260,000	31,000
Maintenance and Inspections[a]:		8,000
Relief Valve Inspection		25
Total Costs	1,760,000	197,000

[a] Costs are based on using cost factors from Peters and Timmerhaus (50) and a total fixed capital cost of $1.8 million (1986 basis) (21) for a 10 tons/day ammonia recovery plant.

[b] Computer control costs are determined using cost estimating factors from Valle-Riestra (51).

TABLE 5-15. EQUIPMENT SPECIFICATIONS ASSOCIATED WITH AMMONIA STORAGE SYSTEM

Equipment Item		Equipment Specifications	Reference
VESSELS:			
Storage Tank	Baseline:	10,000 gal Carbon Steel Storage Tank, 250 psig rating	50,52,53,54
	Level #1:	10,000 gal Carbon Steel with 1/8 in. Corrosion Protection 300 psig	
	Level #2:	10,000 gal Type 316 Stainless Steel, 375 psig rating	
PIPING AND VALVES: Pipework	Baseline:	4 in. Schedule 40 Carbon Steel	55
	Level #1:	4 in. Schedule 80 Carbon Steel	
	Level #2:	4 in. Schedule 80 Type 316 Stainless Steel, 100 ft. in Length	
Check Valve	4 in. Vertical Lift Check Valve, Carbon Steel Construction		52,56
Ball Valve	4 in. Class 300, Carbon Steel Body, Monel® Ball and Trim		50,52,56
Excess Flow	4 in. Standard Valve		52
Angle Valve	4 in. Carbon Steel Construction		57
Relief Valve	2 in. x 3 in. Class 300 Inlet and Outlet Flange, Angle Body, Closed Bonnet with Screwed Cap, Carbon Steel Body		52
Reduced Pressure Valve	Double Check Valve Type Service with Internal Air Gap and Relief Valve		50
Rupture Disk	2 in. Monel® Disk and Carbon Steel Holder		53,58,59
PROCESS MACHINERY:			
Centrifugal Pump	Baseline:	Single Stage, Carbon Steel Construction, Stuffing Box	52,60
	Level 1:	Single Stage, Type 316 Stainless Steel Construction, Double Mechanical Seal	52,60
	Level 2:	Type 316 Stainless Steel Construction, Magnetically-Coupled	52,60

(Continued)

TABLE 5-15 (Continued)

Equipment Item	Equipment Specifications	Reference
INSTRUMENTATION:		
Pressure Gauge	Diaphragm Sealed, Hastelloy C Diaphragm, 0-1,000 psi	
Liquid Level Gauge	Differential Pressure Type	50,61
Temperature Indicator	Thermocouple, Thermowell, Electronic Indicator	50,52,61
Flow Indicator	Differential Pressure Cell and Transmitter and Associated Flowmeter	50,61
Level Indicator	Differential Pressure Type Indicator	50,52,61
Load Cell	Electronic Load Cell	50,61,62
High-low Level Shutoff	Solenoid Valve, Switch, and Relay System	50,52,61
ENCLOSURE:		
Building	Level #1: 26-Gauge Steel Walls and Roof, Door, Ventillation System	57
	Level #2: 10 in. Concrete Walls, 26-Gauge Steel Roof	64
SCRUBBER:	Level #1 and 2: Spray Tower, Monel® Construction, 4 ft. x 12 ft., Water Sprays	
DIKING:	Level #1: 6 in. Concrete Walls, 3 ft. high	57
	Level #2: 10 in. Concrete Walls, Top of Tank Height	

TABLE 5-16. MATERIAL AND LABOR COSTS ASSOCIATED WITH BASELINE AMMONIA STORAGE SYSTEM

	Materials Cost	Labor Cost	Direct Costs	Indirect Costs	Capital Cost
			(1986 $)		
Vessels:					
Storage Tank	86,000	39,000	125,000	44,000	186,000
Piping and Valves:					
Pipework	900	2,100	3,000	1,100	4,500
Check Valves	320	30	350	120	520
Ball Valves (5)	2,000	150	2,150	750	3,200
Excess Flow Valves (2)	600	40	640	220	950
Angle Valves (2)	2,400	40	2,440	860	3,600
Relief Valve	1,300	50	1,330	460	2,000
Process Machinery:					
Centrifugal Pump	4,900	2,100	7,000	2,500	11,000
Instrumentation:					
Pressure Gauges (4)	800	200	1,000	350	1,500
Liquid Level Gauge	800	200	1,000	350	1,500
Total Costs	100,000	44,000	144,000	50,000	215,000

TABLE 5-17. MATERIAL AND LABOR COSTS ASSOCIATED WITH LEVEL 1 AMMONIA STORAGE SYSTEM

	Materials Cost	Labor Cost	Direct Costs	Indirect Costs	Capital Cost
			(1986 $)		
Vessels:					
Storage Tank	102,000	46,000	148,000	52,000	220,000
Piping and Valves:					
Pipework	5,300	2,500	7,800	2,700	12,000
Check Valves	640	60	700	250	1,100
Ball Valves (5)	2,000	150	2,150	750	3,200
Excess Flow Valves (2)	600	40	640	220	950
Angle Valves (2)	2,400	40	2,440	860	3,600
Relief Valve (2)	2,600	100	2,660	920	4,000
Process Machinery:					
Centrifugal Pump	9,300	4,000	13,300	4,700	20,000
Instrumentation:					
Pressure Gauges (4)	800	200	1,000	350	1,500
Flow Indicator	2,000	500	2,500	880	3,700
Liquid Level Gauge	800	200	1,000	350	1,500
Remote Level Indicator	1,000	250	1,250	440	1,900
Enclosures:					
Steel Building	4,600	2,300	6,900	2,400	10,000
Scrubbers:					
Water Scrubber	125,000	56,000	181,000	63,000	268,000
Diking:					
3 ft. High Concrete Diking	390	520	900	320	1,300
Total Costs	259,000	113,000	372,000	130,000	553,000

TABLE 5-18. MATERIAL AND LABOR COSTS ASSOCIATED WITH LEVEL 2 AMMONIA STORAGE SYSTEM

	Materials Cost	Labor Cost	Direct Costs	Indirect Costs	Capital Cost
			(1986 $)		
Vessels:					
Storage Tank	407,000	183,000	590,000	207,000	877,000
Piping and Valves:					
Pipework	1,400	2,600	4,000	1,400	6,000
Reduced Pres. Device	1,600	200	1,800	630	2,700
Ball Valves (5)	2,000	150	2,150	750	3,200
Excess Flow Valves (2)	600	40	640	220	950
Angle Valves (2)	2,400	40	2,440	860	3,600
Relief Valve (2)	2,600	100	2,660	920	4,000
Rupture Disks (2)	650	75	725	250	1,100
Process Machinery:					
Centrifugal Pump	15,000	6,400	21,400	7,500	32,000
Instrumentation:					
Temperature Indicator	1,200	300	1,500	530	2,200
Pressure Gauges (6)	1,200	300	1,500	530	2,200
Flow Indicator	2,000	500	2,500	880	3,700
Load Cell	8,400	2,100	10,500	3,700	16,000
Remote Level Indicator	1,000	250	1,250	440	1,900
Level Alarm	400	100	500	180	740
High-Low Level Shutoff	1,000	250	1,250	440	1,900
Enclosures:					
Concrete Building	6,100	6,600	12,700	4,500	19,000
Scrubbers:					
Water Scrubber	125,000	56,000	181,000	63,000	268,000
Diking:					
10 ft. High Concrete Dike	2,200	2,850	5,000	1,800	7,400
Total Costs	582,000	262,000	844,000	295,000	1,254,000

TABLE 5-19. EQUIPMENT SPECIFICATIONS ASSOCIATED WITH WASTE WATER TREATMENT AMMONIA STRIPPING PROCESS

Equipment Item	Equipment Specification	Reference
VESSELS AND MACHINERY:	Ammonia Stripper and Associated Reboiler and Condenser as Defined in Reference	21
PIPING AND VALVES:		
Pipework	Baseline: 4 in. Schedule 40 Carbon Steel, 360 ft. Level #1: Schedule 80 Carbon Steel Level #2: Schedule 80 Type 316 Stainless Steel	55
Relief Valve	2 in. x 3 in. Class 300 Inlet and Outlet Flanges, Angle Body, Closed Bonnet with Screwed Cap, Carbon Steel Body	52
Rupture Disk	2 in. Monel® Disk and Carbon Steel Holder	53,58,59
INSTRUMENTATION:		
Temp. Sensor	Thermocouple and Associated Thermowell	50,52,61
Temp. Alarm	Indicating and Audible Alarm	51,58,63
Temp. Switch	Two-Stage Switch with Independently Set Actuation	50,61
Remote Temp. Indicator	Transmitter and Associated Electronic Indicator	50,61
Remote Press. Indicator	Transducer, Transmitter and Electronic Indicator	50,61
Flow Control Loop	4 in. Globe Control Valve, Flowmeter and PID Controller	50,61
Flow Interlock System	Solenoid Valve, Switch, and Relay System	50,52,57,61
DIKING:		
	Level #1: 6 in. High Concrete Curbing	57
	Level #2: 3 ft. High Concrete Retaining Wall	
SCRUBBER:	Level #1 and #2: Spray Tower, Monel® Construction 4 ft. x 12 ft., Water Sprays	64

TABLE 5-20. MATERIAL AND LABOR COSTS ASSOCIATED WITH BASELINE WASTE WATER TREATMENT AMMONIA STRIPPER

	Materials Cost	Labor Cost	Direct Costs	Indirect Costs	Capital Cost
			(1986 $)		
Equipment:					
Vessels and Machinery:					
Stripping column					
Reboiler and Condenser					
Centrifugal Pumps (3)					
Total Ves. and Mach.[a]	125,000	56,000	181,000	45,000	260,000
Piping and Valves:[a]	45,000	37,000	82,000	20,000	117,000
Instrumentation:[a]	28,000	9,000	37,000	9,000	53,000
Total Costs	198,000	102,000	300,000	74,000	430,000

[a] Costs are based on using cost factors from Peters and Timmerhaus (50) and a total fixed capital cost of $1.8 million (1986 basis) (21) for a 10 tons/day ammonia recovery plant.

TABLE 5-21. MATERIAL AND LABOR COSTS ASSOCIATED WITH LEVEL 1 WASTE WATER TREATMENT AMMONIA STRIPPER

	Materials Cost	Labor Cost	Direct Costs	Indirect Costs	Capital Cost
			(1986 $)		
Equipment:					
Vessels and Machinery:					
Stripping column					
Reboiler and Condenser					
Centrifugal Pumps (3)					
Total Ves. and Mach.[a]	226,000	101,000	327,000	82,000	470,000
Piping and Valves:[a]	77,000	25,000	102,000	25,000	146,000
Relief Valve	1,300	50	1,350	340	2,000
Instrumentation:[a]	28,000	9,000	37,000	9,000	53,000
Temperature Sensor	200	50	250	60	360
Temperature Alarm	200	50	250	60	360
Remote Temp. Indicator	1,000	250	1,250	310	1,800

(Continued)

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[a] Costs are based on using cost factors from Peters and Timmerhaus (50) and a total fixed capital cost of $1.8 million (1986 basis) (21) for a 10 tons/day ammonia recovery plant.

TABLE 5-21 (Continued)

	Materials Cost	Labor Cost	Direct Costs	Indirect Costs	Capital Cost
			(1986 $)		
Remote Press. Indicator	1,000	250	1,250	310	1,800
Flow Control Loops (2)	6,000	1,500	7,500	1,900	11,000
Diking:					
Curbing Around Reactor	500	350	850	210	1,200
Scrubber:					
Water Scrubber	125,000	56,000	181,000	45,000	260,000
Total Costs	466,000	194,000	660,000	164,000	948,000

TABLE 5-22. MATERIAL AND LABOR COSTS ASSOCIATED WITH LEVEL 2 WASTE WATER TREATMENT AMMONIA STRIPPER

	Materials Cost	Labor Cost	Direct Costs	Indirect Costs	Capital Cost
			(1986 $)		
Equipment:					
Vessels and Machinery:					
Stripping column					
Reboiler and Condenser					
Centrifugal Pumps (3)					
Total Ves. and Mach.[a]	504,000	226,000	730,000	182,000	1,049,000
Piping and Valves:[a]	87,000	29,000	116,000	29,000	167,000
Relief Valve (2)	5,000	100	5,100	1,300	7,400
Rupture Disk (2)	1,500	100	1,600	400	2,300
Instrumentation:[a]	28,000	9,000	37,000	9,000	53,000
Temperature Sensor	200	50	250	60	360
Temperature Alarm	200	50	250	60	360

(Continued)

[a] Costs are based on using cost factors from Peters and Timmerhaus (50) and a total fixed capital cost of $1.8 million (1986 basis) (21) for a 10 tons/day ammonia recovery plant.

TABLE 5-22 (Continued)

	Materials Cost	Labor Cost	Direct Costs	Indirect Costs	Capital Cost
			(1986 $)		
Temperature Switch	300	75	375	95	540
Remote Temp. Indicator	1,000	250	1,250	310	1,800
Remote Press. Indicator	1,000	250	1,250	310	1,800
Flow control Loops (2)	6,000	1,500	7,500	1,900	11,000
Flow Interlock System	1,000	250	1,250	310	1,800
All Loops on Computer Control[b]	105,000	35,000	140,000	35,000	201,000
Diking:					
3 ft. high retaining wall	900	1,200	2,100	530	3,000
Scrubber:					
Water Scrubber	125,000	56,000	181,000	45,000	260,000
Total Costs	866,000	359,000	1,225,000	305,000	1,760,000

[b] Computer control costs are determined using cost estimating factors from Valle-Riestra (51).

TABLE 5-23. FORMAT FOR TOTAL FIXED CAPITAL COST

Item No.	Item	Cost
1	Total Material Cost	-
2	Total Labor Cost	-
3	Total Direct Cost	Items 1 + 2
4	Indirect Cost Items (Engineering & Construction Expenses)	0.35 x Item 3[a]
5	Total Bare Module Cost	Items (3 + 4)
6	Contingency	(0.05 x Item 5)[b]
7	Contractor's Fee	0.05 x Item 5
8	Total Fixed Capital Cost	Items (5 + 6 + 7)

[a] For storage facilities, the indirect cost factor is 0.35. For process facilities, the indirect cost factor is 0.25.

[b] For storage facilities, the contingency cost factor is 0.05. For process facilities, the contingency cost factor is 0.10.

The computation of total fixed capital as shown in Table 5-23 begins with the total direct cost for the system under consideration. This total direct cost is the total direct installed cost of all capital equipment comprising the system. Depending on the specific equipment item involved, the direct capital cost was available or was derived from uninstalled equipment costs by computing costs of installation separately. To obtain the total fixed capital cost, other costs obtained by utilizing factors are added to the total direct costs.

The first group of other cost elements is indirect costs. These include engineering and supervision, construction expenses, and various other expenses such as administration expenses, for example. These costs are computed by multiplying total direct costs by a factor shown in Table 5-23. The factor is approximate, is obtained from the cost literature, and is based on previous experience with capital projects of a similar nature. Factors can have a range of values and vary according to technology area and for individual technologies within an area. Appropriate factors were selected for use in this report based on judgement and experience.

When the indirect costs are added to the total direct costs, total bare module cost is obtained. Some additional cost elements such as contractor's fee and contingency are calculated by applying and adding appropriate factors to the total bare module cost as shown in Table 5-23 to obtain the total fixed capital cost.

Annual Cost--Annual costs are obtained for each of the equipment items by applying a factor for both capital recovery and for maintenance expenses to the direct cost of each equipment item. Table 5-24 defines the cost elements and appropriate factors comprising these costs. Additional annual costs are incurred for procedural items such as valve and vessel inspections, for example. When all of these individual costs are added, the total annual cost is obtained.

TABLE 5-24. FORMAT FOR TOTAL ANNUAL COST

Item No.	Item	Cost
1	Total Direct Cost	-
2	Capital Recovery on Equipment Items	0.163 x Item 1
3	Maintenance Expense on Equipment Items	0.01 x Item 1
4	Total Procedural Items	-
5	Total Annual Cost	Items (2 + 3 + 4)

Sources of Information--

The costs presented in this report are derived from cost information in existing published sources and also from recent vendor information. It was the objective of this effort to present cost levels for ammonia process and storage facilities using the best costs for available sources. The primary sources of cost information are Peters and Timmerhaus (50), Chemical Engineering (65), and Valle-Riestra (51) supplemented by other sources and references where necessary. Adjustments were made to update all costs to a June 1986 dollar basis. In addition, for some equipment items, well-documented costs were not available and they had to be developed from component costs.

Costs in this document reflect the "typical" or "average" representation for specific equipment items. This restricts the use of data in this report to:

- Preliminary estimates used for policy planning,
- Comparison of relative costs of different levels or systems, and
- Approximations of costs that might be incurred for a specific application.

The costs in this report are considered to be "order of magnitude" with a ±50 percent margin. This is because the costs are based on preliminary estimates and many are updated from literature sources. Large departures from the design basis of a particular system presented in this manual or the advent of a different technology might cause the system cost to vary by a greater extent than this. If used as intended, however, this document will provide a reasonable source of preliminary cost information for the facilities covered.

When comparing costs in this manual to costs from other references, the user should be sure the design bases are comparable and that the capital and annual costs as defined here are the same as the costs being compared.

Cost Updating--

All costs in this report are expressed in June 1986 dollars. Costs reported in the literature were updated using cost indices for materials and labor.

Costs expressed in base year dollars may be adjusted to dollars for another year by applying cost indices as shown in the following equation:

$$\text{new base year cost} = \text{old base year cost} \times \frac{\text{new base year index}}{\text{old base year index}}$$

The Chemical Engineering (CE) Plant Cost Index was used in updating cost for this report. For June 1986, the index is 316.3.

Equipment Costs--

Most of the equipment costs presented in this manual were obtained directly from literature sources of vendor information and correspond to a specific design standard. Special cost estimating techniques, however, were used in determining the costs associated with vessels, piping systems, scrubbers, diking, and enclosures. The techniques used are presented in the following subsections of this manual.

Vessels--The total purchased cost for a vessel, as dollars per pound of weight of fabricated unit f.o.b. with carbon steel as the basis (January 1979 dollars) were determined using the following equation from Peters and Timmerhaus (50):

$$\text{Cost} = [50(\text{Weight of Vessel in Pounds})^{-0.34}]$$

The vessel weight is determined using appropriate design equations as given by Peters and Timmerhaus (50) which allow for wall thickness adjustments for corrosion allowances, for example. The vessel weight is increased by a factor of 0.15 for horizontal vessels and 0.20 for vertical vessels to account for the added weight due to nozzles, manholes, and skirts or saddles. Appropriate factors are applied for different materials of construction as given in Peters and Timmerhaus (50). The vessel costs are updated using cost factors. Finally a shipping cost amounting to 10 percent of the purchased cost is added to obtain the delivered equipment cost.

Piping--Piping costs were obtained using cost information and data presented by Yamartino (55). A simplified approach is used in which it is assumed that a certain length of piping containing a given number of valves, flanges, and fittings is contained in the storage or process facility. the data presented by Yamartino (55) permit cost determinations for various lengths, sizes, and types of piping systems. Using these factors, a representative estimate can be obtained for each of the storage and process facilities.

Diking--Diking costs were estimated using Mean's Manual (57) for reinforced concrete walls. The following assumptions were made in determining the costs. The dike contains the entire contents of a tank in the event of a leak or release. Two dike sizes are possible: a three-foot high dike, six-inches thick and a top-of-tank height dike ten inches thick. The tanks are raised off the ground and are not volumetrically included in the volume enclosed by the diking. These assumptions facilitate cost determination for any size diking system.

Enclosures--Enclosure costs were estimated using Mean's Manual (57) for both reinforced concrete and steel-walled buildings. The buildings are assumed to enclose the same area and volume as the top-of-tank height dikes. The concrete building is ten-inches thick with a 26-gauge steel roof and a metal door. The steel building has 26 gauge roofing and siding and metal door. The cost of a ventilation system was determined using a typical 1,000 scfm unit and doubling the cost to account for duct work and requirements for the safe enclosure of hazardous chemicals.

Scrubbers--Scrubber costs were estimated using the following equation from the Gard (64) manual for spray towers based on the actual cubic feet per minute of flow at a chamber velocity of 600 feet/minute.

$$\text{Costs} = 0.235 \times (\text{ACFM} + 43{,}000)$$

A release rate of 10,000 ft^3/minute was assumed for the storage vessel systems and an appropriate rate was determined for process system based on the quantity of hazardous chemicals present in the system at any one time. For the ammonia stripper system, a release rate of 10,000 ft^3/minute was assumed. In addition to the spray tower, the costs also include pumps and a storage tank for the scrubbing medium. The costs presented are updated to June 1986 dollars.

Installation Factors--

Installation costs were developed for all equipment items included in both the process and storage systems. The costs include both the material and labor costs for installation of a particular piece of equipment. The costs were obtained directly from literature sources and vendor information or indirectly by assuming a certain percentage of the purchased equipment cost through the use of estimating factors obtained from Peters and Timmerhaus (50) and Valle-Riestra (51). Table 5-25 lists the cost factors used or the reference from which the cost was obtained directly. Many of the costs obtained from the literature were updated to June 1986 dollars using a 10 percent per year rate of increase for labor and cost indices for materials associated with installation.

TABLE 5-25. FORMAT FOR INSTALLATION COSTS

Equipment Item	Factor or Reference
Vessels:	
Storage Tank	0.45
Expansion Tank	0.25
Piping and Valves:	
Pipework	Ref. 55
Expansion Loop	Ref. 52
Reduced Pressure Device	Ref. 52
Check Valves	Ref. 52
Gates Valves	Ref. 52
Ball Valves	Ref. 52
Excess Flow Valves	Ref. 52
Angle Valves	Ref. 57
Relief Valves	Ref. 52
Rupture Disks	Ref. 52
Process Machinery:	
Centrifugal Pump	0.43
Gear Pump	0.43
Instrumentation:	
All Instrumentation Items	0.25
Enclosures:	Ref. 57
Diking:	Ref. 57
Scrubbers:	0.45

SECTION 6

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APPENDIX A

GLOSSARY

This glossary defines selected terms used in the text of this manual which might be unfamiliar to some users or which might be used differently by different authors.

Accidental release: The unintentional spilling, leaking, pumping, purging, emitting, emptying, discharging, escaping, dumping, or disposing of a toxic material into the environment in a manner that is not in compliance with a plant's federal, state, or local environmental permits and results in toxic concentrations in the air that are a potential health threat to the surrounding community.

Assessment: The process whereby the hazards which have been identified are evaluated in order to provide an estimate for the level of risk.

Cavitation: The formation and collapse of vapor bubbles in a flowing liquid. Specifically the formation and collapse of vapor cavities in a pump when there is sufficient resistance to flow at the inlet side.

Containment/control: A system to which toxic emissions from safety relief discharges are routed to be controlled. A caustic scrubber and/or flare can be containment/control devices. These systems may serve the dual function of destructing continuous process exhaust gas emissions.

Creep failure: Failure of a piece of metal as a result of creep. Creep is time dependent deformation as a result of stress. Metals will deform when exposed to stress. High levels of stress can result in rapid deformation and rapid failure. Lower levels of stress can result in slow deformation and protracted failure.

Deadheading: Closing or nearly closing or blocking the discharge outlet or piping of an operating pump or compressor.

Electromotive Series of Metals: A list of metals and alloys arranged according to their standard electrode potentials; which also reflects their relative corrosion potential.

Enthalpy: A thermodynamic property of a chemical related to its energy content at a given condition of temperature, pressure and physical state. Enthalpy is the internal energy added to the product of pressure times volume. Numerical values of enthalpy for various chemicals are always based on the change in enthalpy from an arbitrary reference pressure and temperature, and physical state, since the absolute value cannot be measured.

Facility: A location at which a process or set of processes are used to produce, refine or repackage chemicals, or a location where a large enough inventory of chemicals are stored so that a significant accidental release of a toxic chemical is possible.

Hazard: A source of danger. The potential for death, injury or other forms of damage to life and property.

Hygroscopic: Readily absorbing and retaining moisture, usually in reference to readily absorbing moisture from the air.

Identification: The recognition of a situation, its causes and consequences relating to a defined potential, e.g. Hazard Identification.

Mild steel: Carbon steel containing a maximum of about 0.25% carbon. Mild steel is satisfactory for use where severe corrodants are not encountered or where protective coatings can be used to prevent or reduce corrosion rates to acceptable levels.

Mitigation: Any measure taken to reduce the severity of the adverse effects associated with the accidental release of a hazardous chemical.

Olefinic hydrocarbons: A specific subgroup of aliphatic hydrocarbons sharing the common characteristic of at least one unsaturated carbon-to-carbon atomic bond in the hydrocarbon molecule, and with straight or branched chain structure.

Passivation film: A layer of oxide or other chemical compound of a metal on its surface that acts as a protective barrier against corrosion or further chemical reaction.

Plant: A location at which a process or set of processes are used to produce, refine, or repackage, chemicals.

Prevention: Design and operating measures applied to a process to ensure that primary containment of toxic chemicals is maintained. Primary containment means confinement of toxic chemicals within the equipment intended for normal operating conditions.

Primary Containment: The containment provided by the piping, vessels and machinery used in a facility for handling chemicals under normal operating conditions.

Probability/potential: A measure, either qualitative or quantitative, that an event will occur within some unit of time.

Process: The sequence of physical and chemical operations for the production, refining, repackaging or storage of chemicals.

Process machinery: Process equipment, such as pumps, compressors, heaters, or agitators, that would not be categorized as piping and vessels.

Protection: Measures taken to capture or destroy a toxic chemical that has breached primary containment, but before an uncontrolled release to the environment has occurred.

Qualitative Evaluation: Assessing the risk of an accidental release at a facility in relative terms; the end result of the assessment being a verbal description of the risk.

Quantitative Evaluation: Assessing the risk of an accidental release at a facility in numerical terms; the end result of the assessment being some type of number reflects risk, such as faults per year or mean time between failure.

Reactivity: The ability of one chemical to undergo a chemical reaction with another chemical. Reactivity of one chemical is always measured in reference to the potential for reaction with itself or with another chemical. A chemical is sometimes said to be "reactive", or have high "reactivity", without reference to another chemical. Usually this means that the chemical has the ability to react with common materials such as water, or common materials of construction such as carbon steel.

Redundancy: For control systems, redundancy is the presence of a second piece of control equipment where only one would be required. The second piece of equipment is installed to act as a backup in the event that the primary piece of equipment fails. Redundant equipment can be installed to backup all or selected portions of a control system.

Risk: The probability that a hazard may be realized at any specified level in a given span of time.

Secondary Containment: Process equipment specifically designed to contain material that has breached primary containment before the material is released to the environment and becomes an accidental release. A vent duct and scrubber that are attached to the outlet of a pressure relief device are examples of secondary containment.

Toxicity: A measure of the adverse health effects of exposure to a chemical.

APPENDIX B

TABLE B-1. METRIC (SI) CONVERSION FACTORS

Quantity	To Convert From	To	Multiply By
Length:	in	cm	2.54
	ft	m	0.3048
Area:	in^2	cm^2	6.4516
	ft^2	m^2	0.0929
Volume:	in^3	cm^3	16.39
	ft^3	m^3	0.0283
	gal	m^3	0.0038
Mass (weight):	lb	kg	0.4536
	short ton (ton)	Mg	0.9072
	short ton (ton)	metric ton (t)	0.9072
Pressure:	atm	kPa	101.3
	mm Hg	kPa	0.133
	psia	kPa	6.895
	psig	kPa*	((psig)+14.696)x(6.895)
Temperature:	°F	°C*	(5/9)x(°F-32)
	°C	K*	°C+273.15
Caloric Value;	Btu/lb	kJ/kg	2.326
Enthalpy:	Btu/lbmol	kJ/kgmol	2.326
	kcal/gmol	kJ/kgmol	4.184
Specific-Heat Capacity:	Btu/lb-°F	kJ/kg-°C	4.1868
Density:	lb/ft^3	kg/m^3	16.02
	lb/gal	kg/m^3	119.8
Concentration:	oz/gal	kg/m^3	7.490
	quarts/gal	cm^3/m^3	25,000
Flowrate:	gal/min	m^3/min	0.0038
	gal/day	m^3/day	0.0038
	ft^3/min	m^3/min	0.0283
Velocity:	ft/min	m/min	0.3048
	ft/sec	m/sec	0.3048
Viscosity:	centipoise (CP)	kg/m-s	0.001

*Calculate as indicated